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Rafulla Chandra Ray

To

SIR PRAFULLA CHANDRA RÂY, KT., C.I.E., D.Sc., PH.D.

REVERED SIR,

In presenting this Jubilee Volume to you, the Council of the Indian Chemical Society recalls with pleasure and gratitude your valuable services to the cause of science in this land of ours. You have been a pioneer of chemical research in India, both pure and applied, and it is no exaggeration to say that Indian Chemists of to-day owe their inspiration, either directly or indirectly to you. Your pioneering work on the history of Hindu Chemistry has helped the world to realise that the contribution of the Hindus to the early developments of the chemical and medical sciences is second to that of no other people.

The Indian Chemical Society has found in you one who has always been willing to assist it in every way possible. But for your munificence, the Society would not be in its present position, and would have had to restrict its activities in many directions. Your philanthropy and spirit of self sacrifice, almost unique, has brought within the scope of your activities successful organisation of relief of distress caused by flood and famine, unfortunately much too frequent in this country. Your keen interest in the burning social and economic problems of the day tempered by your mature judgment and devotion to the service of Mother India, have made your name a household word. May you live long to inspire the youths of this country and to elevate them morally and intellectually to their ordained destiny!

Yours sincerely

FELLOWS OF THE INDIAN CHEMICAL SOCIETY



## Dehydrogenation of Pyridine by Anhydrous Metallic Chlorides.

By GILBERT T. MORGAN AND FRANCIS HEREWARD BURSTALL.

In pursuance of our researches on co-ordination compounds it became desirable to obtain considerable quantities of 2:2'-dipyridyl (dipy, formula I) because of the interest attaching to combinations of this powerful chelating diamine with various metallic salts. It will be recalled that in 1912 A. Werner resolved into optically active enantiomers the dark red complex salt  $[\text{Fe } 3\text{dipy}] \text{Br}_3 \cdot 6\text{H}_2\text{O}$ , thus demonstrating an octahedral arrangement of the three chelate groups round the central ferrous radical (*Ber.*, 1912, **45**, 484). More recently we have resolved the analogous pink complex nickel salt  $[\text{Ni } 3\text{dipy}] \text{Cl}_3 \cdot 6\text{H}_2\text{O}$  into *dextro*- and *laevo*-forms thereby bringing the stereochemistry of nickelous salts into line with that of the ferrous series (Morgan and Burstall, *J. Chem. Soc.*, 1931, 2213).

2:2'-Dipyridyl has also proved useful in stabilising the higher valency of silver for it has given rise to the following complex salts of bivalent silver *viz.*,  $[\text{Ag } 2\text{dipy}] \text{S}_2\text{O}_8$ ,  $[\text{Ag } 3\text{dipy}] \text{X}_2$ , where  $\text{X} = \text{NO}_3$ ,  $\text{ClO}_3$  or  $\text{ClO}_4$  (Morgan and Burstall, *J. Chem. Soc.*, 1930, 2594). These preparations were supplied to Professor S. Sugden who by a study of their magnetic properties showed that the diadic silver radical is in an electronic condition similar to that which obtains in the copper radical of cupric salts. The commonly occurring salts of univalent silver are uniformly diamagnetic but Sugden's experiments indicate plainly that foregoing series of complex salts of bivalent silver are all distinctly paramagnetic and closely comparable in this respect with cupric salts (*Nature*, 1931, **128**, 31; *J. Chem. Soc.*, 1932, 161).

Of the various methods available for the production of 2:2'-dipyridyl the most practicable for large scale preparations appeared to

be a process devised by Hein and Retter (*Ber.*, 1928, **61**, 1790) who heated pyridine with anhydrous ferric chloride in sealed tubes at 300° for about 35 hours. When operating with 70 g. of pyridine and 13 g. of ferric chloride these investigators recorded the production of good yields of 2:2'-dipyridyl but without mentioning the formation of any by-products.

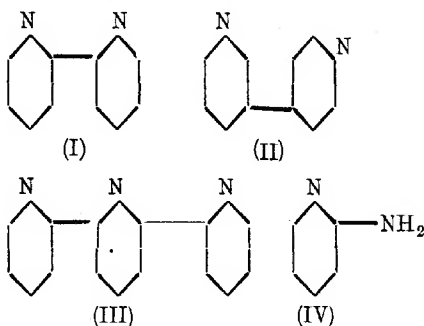
We have repeated this mode of dehydrogenation with quantities of pyridine ranging from one to eight litres when favourable yields of 2:2'-dipyridyl were obtained. We also isolated and identified some 20 other products arising from complicated and far reaching chemical changes which take place under drastic conditions approximating to the critical temperature and pressure of pyridine. Our detailed examination of this complicated mixture of bases has already been recorded (Morgan and Burstall, *J. Chem. Soc.*, 1932, 20). The following list is probably not complete although the major constituents of the mixture have been identified.

<i>Alkylated pyridines.</i>	<i>Dipyridyls.</i>	<i>Other bases.</i>
3-Methylpyridine	2:2'-Dipyridyl	Ammonia
4-Methylpyridine	3:4'-Dipyridyl	2-Aminopyridine
2-Ethylpyridine	2:3'-Dipyridyl	2:2'-Dipiperidyl
3-Ethylpyridine	2:4'-Dipyridyl	3:4'-Dipiperidyl
4-Ethylpyridine	3:3'-Dipyridyl	Base, m. p. 120°
2:3-Dimethylpyridine		Base, m. p. 214°
3:4-Dimethylpyridine	<i>Tripyridyls.</i>	
2 <i>iso</i> Propylpyridine	2:2':2''-Tripyridyl	Resinamines
x:x-Diethylpyridine	2:2':x''-Tripyridyl	

From the foregoing schedule it will be seen that the most outstanding result of our extension of Hein and Retter's process is the discovery of isomeric tripyridyls and to the more abundant of these triamines we have ascribed the formula (III) on account of its behaviour in co-ordination.

In the hope of increasing the yields of 2:2'-dipyridyl and 2:2':2''-tripyridyl (bis-2-pyridyl-2:6-pyridine) we have experimented with five other anhydrous metallic chlorides instead of ferric chloride and as a variant of the original method we have also employed pyridine

ferrichloride  $C_5H_5N$ ,  $HFeCl_4$ . The results of these dehydrogenations may now be reviewed in turn.



*Cobaltic chloride.* As cobaltic chloride cannot be used as such we prepared the stable green tetrapyridinodichlorocobaltic chloride  $[CoCl_2 4py] Cl$ , which was first recorded by Werner and Feenstra (*Ber.*, 1906, **39**, 1538). Alkylated pyridines and 2-aminopyridine (IV) are formed as in the case of ferric chloride but in the dipyridyl series the yields of 2:2'-dipyridyl (I) and 3:4'-dipyridyl (II) are much higher (Table I) whereas 3:3'-dipyridyl, 4:4'-dipyridyl and dipiperidyls are not formed. It is noteworthy that very little 2:2':2''-tripyridyl (bis-2-pyridyl-2:6-pyridine III) is produced. The large proportions of non-crystallisable resinamines and of carbonaceous matter indicate extensive "cracking."

*Cupric chloride.* Cupric chloride was used in the form of dipyridino cupric chloride  $[CuCl_2 2py]$  which is easily obtained from pyridine and cupric chloride (compare Matthews and Spero, *J. Phys. Chem.*, 1917, **21**, 402). Dehydrogenation of pyridine with this chloride requires but little comment. The two most plentiful dipyridyls, 2:2'-dipyridyl and 3:4'-dipyridyl were identified. 2-Aminopyridine was also produced and in larger quantity than in any of the other experiments (See Table I).

*Tungsten hexachloride.* This higher chloride like the two following metallic chlorides caused extensive rupture of the pyridine molecule with consequent formation of a large quantity of non-crystallisable resinamines and carbonaceous matter. 2-Aminopyridine, 2:2'-dipyridyl and 3:4'-dipyridyl were nevertheless identified.

It has been shown by Cooper and Wardlaw (*J. Chem. Soc.*, 1932, 635) that pyridine and tungsten hexachloride give the compound  $(C_5H_5N)_2 WOCl_5 \cdot H_2O$  which contains pentavalent tungsten, but

this substance is formed at ordinary temperature, and in presence of moisture.

*Molybdenum pentachloride.* The products from this dehydrogenation are similar to those of the foregoing experiment; 2-aminopyridine, 2:2'-dipyridyl and 3:4'-dipyridyl are the only substances obtained in a state of purity. It is noteworthy that Wardlaw and Webb (*J. Chem. Soc.*, 1930, 2100) obtained compounds of the type  $\text{MoCl}_4 \cdot n\text{C}_5\text{H}_5\text{N}$  (where  $n = 3, 4$  and  $5$ ) from the pentachloride and pyridine, but without mentioning products of dehydrogenation.

*Stannic chloride.* In this dehydrogenation the three most easily identified compounds are isolated, namely, 2-aminopyridine, 2:2'-dipyridyl and 3:4'-dipyridyl. Very extensive "cracking" is apparent from the large quantity of resinamines and insoluble residue produced in this reaction.

This employment of the three foregoing higher chlorides does not lead to any increased yield of desirable products.

*Pyridine ferrichloride,  $\text{C}_5\text{H}_5\text{N} \cdot \text{HFeCl}_4$ .* This salt, which is readily prepared by mixing its generators in hydrochloric acid, possesses certain advantages over anhydrous ferric chloride. It is not hygroscopic and is easily soluble in anhydrous pyridine without development of heat. Moreover it melts at a low temperature ( $125^\circ$ ). The results obtained by heating this salt with pyridine are comparable, in so far as the formation of alkylated pyridines are concerned, with those obtained by the use of ferric chloride. But pyridine ferrichloride gives the largest yield of tripyridyls so far obtained in our dehydrogenation experiments. 2:2':2''-Tripyridyl and its isomeride 2:2':x''-tripyridyl were both identified.

In the following tables which summarise these experiments weights are always recorded in grams (pp. 6 and 7).

*Co-ordination Compounds of 2:2'-Dipyridyl with Bivalent Metals.*

In addition to the 2:2'-dipyridyl complex salts of nickel and bivalent silver already mentioned (p. 1) we have combined this base with compounds of other bivalent metals and the following are now described for the first time.

*Platinous salts.* Although the co-ordination compounds of platinum containing chelate rings have been less extensively studied than the corresponding compounds of cobalt nevertheless certain sulphur containing addenda which are capable of functioning as chelate groups have been utilised by Sir P. C. Rây and his collaborators in their researches on the valencies of platinum (*Proc. Chem. Soc.*,

1914, 30, 304; *J. Chem. Soc.*, 1923, 123, 133, 197; *J. Indian Chem. Soc.*, 1927, 4, 467; *Z. anorg. Chem.*, 1929, 178, 329; *ibid.*, 1930, 187, 33; 1931, 198, 53). The following paragraphs contain a preliminary account of the application of 2:2'-dipyridyl to co-ordination compounds problems in the platinum series.

By operating under varying conditions we have isolated two compounds  $[\text{PtCl}_2 \text{ dipy}]$  which we shall refer to as  $\alpha$ - and  $\beta$ -derivatives as they have the same percentage composition; but we do not commit ourselves to any opinion regarding their molecular complexity. They may be isomeric or alternatively one may be polymeric to the other.

$\alpha$ -2:2'-Dipyridylplatinous chloride is formed as an orange-yellow, crystalline, insoluble salt when molecular quantities of potassium chloroplatinite and 2:2'-dipyridyl are heated in aqueous medium.  $\beta$ -2:2'-Dipyridylplatinous chloride is a primrose yellow compound obtained by the decomposition of a complex substance which crystallises in pale buff needles when aqueous potassium chloroplatinite is added to a solution of 2:2'-dipyridyl dissolved in dilute acetic or hydrochloric acid. These two compounds which retain their distinctive colours on keeping are still under investigation.

*Palladous salt.* Only the derivative of palladous chloride has so far been obtained, namely, 2:2'-dipyridylpalladous chloride  $[\text{PdCl}_2 \text{ dipy}]$  which is readily formed from its generators. There is no appreciable tendency for this complex salt to combine with a further molecule of diamine.

*Manganous salts.* Manganous chloride and 2:2'-dipyridyl react smoothly in aqueous solution with the formation of *tris*-2:2'-dipyridylmanganous chloride  $[\text{Mn } 3\text{dipy}]\text{Cl}_2$  which has been obtained in both anhydrous and hydrated forms. The orange *hydrate* very rapidly loses its combined water, leaving a residue of the yellow anhydrous salt. The corresponding *tris*-2:2'-dipyridylmanganous bromide and iodide have been obtained by double decomposition of the foregoing chloride with a soluble bromide and iodide respectively. The former gives a *heptahydrate*, the latter a *hexahydrate*. These complex manganese salts are less stable than the analogous salts of nickel.

*Copper salt.* Cupric chloride and excess of 2:2'-dipyridyl yield *tris*-2:2'-dipyridylcupric chloride *hexahydrate*  $[\text{Cu } 3\text{dipy}]\text{Cl}_2 \cdot 6\text{H}_2\text{O}$  when mixed in aqueous media. Compounds of copper salts and dipyridyl which contain a smaller amount of the base have previously been recorded by Blau (*Monatsh.*, 1898, 19, 647).



TABLE I.

*Weights of products obtained on using 100 g. of anhydrous chloride.*

Metallic chloride.	Total reac- tion pro- ducts.	Alkyl pyri- dines.	Total pyri- dines.	2,2'-Di- pyridyl.	3,4'-Di- pyridyl.	2-Amino- pyridines.	Total tri- pyridyls.	Resin- amines.	Combustible organic mater.
Ferric chloride*	140.1	16.1	52.1	34.4	4.7	0.63	14.8	38.6	32.1
Cobaltic chloride† (1)	385.1	26.9	86.4	53.6	8.2	0.48	0.8	90.9	155.4
(2)	106.7	20.8	43.1	34.8	2.2	0.3	trace	7.4	35.1
Cupric chloride	92.0	8.2	30.1	20.9	4.5	2.3	1.2	21.2	19.0
Tungsten hexachloride	111.0	12.5	16.6	6.6	0.8	0.33	0.6	21.6	60.0
Molybdenum pentachloride	113.1	25.2	11.6	9.0	1.2	0.9	trace	48.0	27.4
Stannic chloride	186.8	13.0	20.0	8.8	2.1	0.1	0.7	49.0	104.0
Ferric chloride (Pyridine ferrichloride)	233.8	22.5	52.6	23.0	0.3	0.98	24.4	44.8	88.6

The data of the first horizontal column taken from *J. Chem. Soc.*, 1932, 20 are included for comparative purposes.

The second experiment with cobaltic chloride was carried out at 320° for only 18 hours.

TABLE II.

*Weights of materials and products.*

Metallic chloride.	Pyridine.	Metallic chloride.	Pyridine recovered.	Alkylated pyridines, % total.	2:2'-Di-pyridyl.	3:4'-Di-pyridyl.	2-Amino-pyridine.	Tripyridyls.	Resin-amines.	Carbonaceous matter.	
Ferric chloride	8000	1524	5680	245.0	794.0	524.0	72.0	9.6	225.0	512.0	490.0
Cobaltic chloride (1)	8000	2428	5921	224.0	721.0	447.0	68.5	4.0	7.0	758.0	1295.0
(2)	2000	196	1648	14.0	29.0	23.4	1.5	0.2	trace	5.0	23.6
Tungsten hexachloride	550	60	372	7.5	10.0	4.0	0.5	0.2	0.4	13.0	36.1
Molybdenum pentachloride.	550	50	463	12.6	5.8	4.5	0.6	0.46	trace	24.0	13.7
Stannic chloride	400	100	121	13.0	20.0	8.8	2.1	0.1	0.7	49.0	104.0
Cupric chloride	2000	318	1941	12.0	44.0	30.5	6.6	3.4	1.8	31.0	27.7
Pyridine ferrichloride	2000	700	844	92.0	215.0	94.0	1.2	4.0	100.0	183.0	362.0

### EXPERIMENTAL.

The procedure adopted in the following experiments was essentially the same as that followed in our researches on the dehydrogenation of pyridine by anhydrous ferric chloride (Morgan and Burstall, *loc. cit.*). The metallic chloride and an excess of pyridine were placed in the stainless steel container of an autoclave from which air was displaced by carbon dioxide. The mixture was then heated with stirring to the desired temperature for 36 hours. When the autoclave was cooled to room temperature the gases formed during the reaction were drawn off and a sample collected for analysis. The product from the autoclave was then transferred to a still, mixed with water, made alkaline with a small excess of caustic soda and distilled in steam. The first runnings which consisted mainly of unchanged pyridine and alkylpyridines were collected separately; the distillation was then continued until a sample of the distillate no longer gave any colour with ferrous salts. The aqueous distillate was evaporated with excess of hydrochloric acid to crystallising point and the hydrochlorides were mixed with the first runnings of pyridine. The mixture was basified with caustic soda solution, solid alkali being added after neutralisation. The dark brown layer of pyridine and pyridine derivatives was dried over solid caustic soda and finally fractionated under ordinary pressure. Individual compounds were then separated and identified in the manner indicated in each experiment.

#### I. Cobaltic Chloride.

Tetrapyridinodichlorocobaltic chloride  $[\text{CoCl}_2 \cdot 4\text{py}]\text{Cl}$ , was prepared by the method outlined by Werner and Feenstra (*loc. cit.*). Cobaltous chloride was dissolved in one and a half times its weight of water and treated with four molecular equivalents of pyridine. The mixture was heated until a clear deep blue solution was obtained. This liquid was cooled with stirring when a pink crystalline cobaltous salt separated, and on passing chlorine through the mixture, the pink intermediate product speedily dissolved with concurrent formation of green crystals of complex cobaltic salt. When the mixture contained excess of halogen, it was cooled to  $0^\circ$  and the green precipitate collected, pressed and washed with a little cold 2N-hydrochloric acid. A further quantity of the complex cobaltic

chloride was obtained by evaporating the dark brown filtrate and cooling to 0°. Tetrapyridinodichlorocobaltic chloride crystallised with 6H<sub>2</sub>O and the combined water was removed by heating at 110°. The anhydrous chloride was a light bluish green powder. (Found: Co, 12.91. Calc. Co, 12.25 per cent.). Pure dry pyridine (8000 g.) and anhydrous tetrapyridinodichlorocobaltic chloride (2428 g.) were heated at 350° for 36 hours. Analysis of the gas collected showed hydrogen, nitrogen, saturated hydrocarbons (C<sub>n</sub>H<sub>2n+2</sub>, where  $n=1.1$ ) and some of the carbon dioxide reduced to carbon monoxide. The autoclave then contained a dark reddish brown semi-solid mixture.

*Distillate.* The portion of the product volatile in steam gave unchanged pyridine (5921 g.). The next fraction (b.p. 130-250°) contained alkylated pyridines (228 g.) which were separated into ten degree fractions by distillation through a long column. A portion of the product (b.p. 135-145°) was treated with mercuric chloride and dilute hydrochloric acid. The more sparingly soluble white needles proved to be 3-methylpyridine mercurichloride, m.p. 145-46°, while the more soluble part gave 4-methylpyridine mercurichloride, m.p. 128°. The fraction b.p. 160-165° furnished 3-ethylpyridine mercurichloride, m.p. 130° as the main product when treated with mercuric chloride and dilute hydrochloric acid. The fraction b.p. 190-210° was mixed with an equal volume of benzene and extracted with water. Solid caustic soda added to the aqueous extract caused the separation of 2-aminopyridine (4.0 g.) which was dissolved in benzene and the base recovered by distillation. 2-Aminopyridine (m.p. 56°, b.p. 205-07°) was easily soluble in water and gave a picrate, m.p. 217°.

*Dipyridyls.* After removal of the alkylated pyridines dipyridyls and related substances (b.p. 250-310°) distilled over. This fraction (721 g.) was cooled to 0°; when 2:2'-dipyridyl (360 g.) crystallised and was filtered from oily isomerides. The oily filtrate (861 g.) was mixed with benzene and shaken with water when the aqueous extract did not give any 3:3'-dipyridyl or dipiperidyls (compare Morgan and Burstall, *loc. cit.*). The solvent was removed from the oily diamines which were then treated with hydrogen chloride in alcohol. The precipitated hydrochlorides were collected and the bases (210 g.) recovered. The oily bases were then dissolved in benzene and shaken with excess of aqueous ferrous sulphate; the dark red ferrous extract then gave 2:2'-dipyridyl (87 g.) and oily alkylated 2:2'-dipyridyls (46 g.) while the benzene solution after removal of solvent and distillation gave almost pure 3:4'-dipyridyl (68.5 g., m.p. 63°,

picrate, m.p. 215°). The alcoholic solution of bases not precipitated as hydrochlorides by hydrogen chloride, was made alkaline, the bases recovered, dissolved in benzene and treated with aqueous ferrous sulphate. This intense red extract gave a further quantity of alkylated 2:2'-dipyridyls (38 g.) while the benzene solution furnished an oil (72 g.) which probably contained 2:3'- and 2:4'-dipyridyls.

*Residue.* The residue remaining after removal of bases volatile in steam consisted of a dark red solution containing black solid in suspension. This solid was collected and the filtrate evaporated to small volume, treated with solid caustic soda and extracted with benzene. The solvent was removed and the oily residue extracted with petroleum (b.p. 40-60°). Tripyridyls (7.0 g.) were extracted and this mixture of triamines gave pure crystalline 2:2':2''-tripyridyl (4.2 g., m.p. 88-89°).

The residue insoluble in water was dried and extracted in a Soxhlet apparatus with petroleum (b.p. 40-60°) and then with benzene. The petroleum extract gave a brown oil (93 g.) while the benzene solution furnished resinamines (665 g.). Analysis of the residue not soluble in organic solvents showed the presence of 54.9% of combustible matter. This gave a total of 1295 g. of carbonaceous material. Qualitative tests of the inorganic residue showed the presence of iron oxide, this being derived from the steel of the container.

A repetition of the foregoing experiment was made using a smaller quantity of reagents [ $\text{CoCl}_2 \cdot 4\text{py}$ ] $\text{Cl}$ , (196 g.) and pyridine (2000 g.) at a lower temperature (320°) and with shorter period of heating. The results are summarised in Table I.

## II. Cupric Chloride.

Dipyridinocupric chloride [ $\text{CuCl}_2 \cdot 2\text{py}$ ] was prepared by adding cupric chloride ( $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ) to a large excess of pyridine. The bluish green precipitate was collected, air dried and kept in a desiccator (*cf.* Matthews and Spero, *J. Phys. Chem.*, 1917, **21**, 401). Pure pyridine (2000 g.) and dipyridinocupric chloride (318 g.) were heated for 36 hours at 340°. Analysis of the gases collected from the autoclave showed hydrogen, nitrogen, saturated hydrocarbons ( $\text{C}_n\text{H}_{2n+2}$ , where  $n=1-2$ ) and a considerable proportion of the carbon dioxide reduced to carbon monoxide. The dark red semi-solid product dissolved partially in water to a deep crimson solution containing black suspended matter.

*Distillate.* Pyridine (1941 g.) was recovered unchanged. Alkylated pyridines boiled between 130-250° and the whole of this fraction (15·4 g.) was treated with benzene and extracted with water. Excess of picric acid was added to the aqueous extract when 2-aminopyridine picrate (11·8 g.) crystallised. The alkylpyridine fraction (12·0 g.) was not further investigated.

*Dipyridyls.* This portion of the distillate (b.p. 250-310°) (44 g.) gave on cooling 2:2'-dipyridyl (28·5 g.). Precipitation of the hydrochlorides in alcohol gave 3:4'-dipyridyl (4·9 g.). The residual oil after separation of the foregoing bases was treated with a molecular equivalent of alcoholic picric acid. 3:4'-Dipyridyl picrate (4·2 g.) was obtained while the more soluble picrates gave 2:2'-dipyridyl picrate (6·2 g., 2·5 g. base). The remaining picrates were reconverted to bases (5·1 g.) which were then mixed with benzene and treated with aqueous ferrous sulphate. The benzene solution furnished an oil (3·0 g.) while alkylated 2:2'-dipyridyls (1·4 g.) were recovered from the ferrous sulphate extract.

*Residue.* The residue was collected and the filtrate evaporated and treated with solid caustic soda. Benzene extracted an almost black oil (1·8 g.) which gave an intense purple colour with ferrous salts but failed to furnish any crystalline substance. By extraction with benzene the black solid residue (155 g.) provided resins (31 g.). That part of the residue insoluble in organic solvents contained 22·3% of combustible organic matter, giving a total weight of 27·7 g.

### III. Tungsten Hexachloride.

Tungsten hexachloride was prepared by the action of chlorine on heated metallic tungsten (Biltz, "Laboratory Methods of Inorganic Chemistry", p. 231; compare Hill, *J. Amer. Chem. Soc.*, 1916, **38**, 2383; Cooper and Wardlaw, *loc. cit.*). The chloride was obtained in almost black glistening crystals which decrepitated on cooling. Pure pyridine (550 g.) and tungsten hexachloride (60 g.) were carefully mixed with cooling, and then heated for 36 hours at 320°. A sample of gas from the cooled product showed hydrogen, nitrogen, saturated hydrocarbons ( $C_nH_{2n+2}$ , where  $n = 1\cdot1$ ), a trace of olefines and a small proportion of the carbon dioxide reduced to carbon monoxide. The black semi-solid product dissolved in water to a deep crimson solution containing solid in suspension.

*Distillate.* Distillation in steam gave unchanged pyridine (372 g.) and alkylated pyridines (7.7 g.); the latter were washed with water and treated with picric acid, 2-aminopyridine picrate (0.8 g.) was isolated.

*Dipyridyls.* This fraction (10 g., b. p. 250-310°) gave 2:2'-dipyridyl (3.0 g.) on cooling. The residual oil was treated with picric acid in alcohol, and when the solution was concentrated 3:4'-dipyridyl picrate (1.4 g.) separated as the more sparingly soluble fraction, the more soluble 2:2'-dipyridyl picrate (2.5 g.) was obtained on further evaporation and the residual picrates after reconversion into bases gave alkyl-2:2'-dipyridyls (1.3 g.) by extraction with ferrous sulphate leaving a small residue (4.2 g.).

*Residue.* The non-volatile residue was filtered from solid and the red filtrate treated with caustic soda. Benzene extracted mixed oily tripyridyls (0.4 g.) which partly crystallised on long keeping. The crystals were removed by hand and crystallised from petroleum (b. p. 40-60°). A few white needles of a basic substance, m. p. 120° were isolated but the quantity was too small for detailed examination. The black insoluble residue (95 g.) provided resins (13.0 g.) and combustible organic material (36.1 g.).

#### IV. Molybdenum Pentachloride.

Molybdenum pentachloride was prepared by the action of chlorine on heated metallic molybdenum (Blitz, "Laboratory Methods of Inorganic Chemistry", p. 226; compare Wardlaw and Webb, *loc. cit.*).

Pyridine (550 g.) and molybdenum pentachloride (50 g.) were carefully mixed with cooling and the mixture heated for 36 hours at 320°. A gas analysis showed hydrogen, nitrogen, saturated hydrocarbons ( $C_nH_{2n+2}$ ) and carbon dioxide partially reduced to carbon monoxide. The almost black product gave a red solution in water which contained a considerable quantity of insoluble solid. The mixture was worked up in exactly the same manner as that used in the previous experiment. Pyridine recovered (463 g.). Alkylated pyridines (13.1 g.) which also gave 2-aminopyridine picrate (1.6 g., *i.e.*, 0.46 g. base).

*Dipyridyls.* This fraction (5.8 g.) was divided into 2:2'-dipyridyl (4.5 g.) of which 1.0 g. was separated as 2:2'-dipyridyl picrate (2.5 g.). 3:4'-Dipyridyl (0.6 g.) was identified as picrate (1.5 g.) while the oil remaining (0.7 g.) was not investigated further.

*Residue.* Only traces of tripyridyls were found in the liquid residue but the solid portion gave resinamines (24 g.) and combustible organic matter (13.7 g.).

#### V. Stannic Chloride.

Stannic chloride (100 g.) was slowly added to well cooled pyridine (400 g.). A vigorous reaction took place with the formation of an insoluble white powder. The mixture was then treated for 36 hours at 340°. Analysis of the gas showed hydrogen, nitrogen, saturated hydrocarbons ( $C_nH_{2n+2}$ ), and a little carbon dioxide reduced to carbon monoxide. The contents of the autoclave consisted of a little liquid and a large quantity of tough black solid which was only removed from the autoclave with great difficulty. On treatment with water a deep crimson liquid containing much solid in suspension was obtained. The mixture was worked up in a similar manner to that used for experiments III and IV. Pyridine recovered (121 g.); alkylated pyridines (13 g.); 2-aminopyridine (0.4 g. picrate, 0.1 g. base).

*Dipyridyls*, (20 g.), furnished 2:2'-dipyridyl (8.8 g.) and 3:4'-dipyridyl (2.1 g.) and alkylated dipyridyls (5.3 g.).

*Residue.* The water soluble residue gave a liquid tripyridyl fraction (0.7 g.) which did not crystallise. The insoluble residue (320 g.) gave resinamines (49 g.) and combustible organic matter (104 g.).

#### VI. Pyridine Ferrichloride.

Pyridine ferrichloride,  $C_5H_5N \cdot HFeCl_4$ , was obtained by evaporating equimolecular quantities of pyridine and anhydrous ferric chloride in a large excess of hydrochloric acid. The deep red mixture was heated until all water and excess of hydrochloric acid had been removed. On cooling the ferrichloride set to a hard yellow crystalline cake which was broken up to a brown-yellow powder. This soluble salt melted at 125° and was stable above 250°. Moreover it dissolved readily in water, alcohol or anhydrous pyridine but was rather less soluble in benzene, chloroform or acetone. (Found: Fe, 20.8.  $C_5H_6 \cdot NCl_4Fe$  requires Fe, 20.10 per cent.).

Pyridine (2000 g.) and pyridine ferrichloride (700 g.) were heated at 340-350° for 36 hours. Analysis of the gas showed hydrogen, nitrogen, saturated hydrocarbons ( $C_nH_{2n+2}$ , where  $n=1.7$ ) and some carbon dioxide reduced to carbon monoxide. The product in the



autoclave was a partly crystalline, hygroscopic, greenish black solid.

It gave an intense reddish purple solution when treated with water but much black solid remained in suspension. The mixture was worked up according to the method used for experiment I. Pyridine recovered (844 g.) and alkylated pyridines (96 g.), from which 2-aminopyridine (4.0 g.) was extracted, included all fractions boiling up to 250°.

*Dipyridyls* (215 g.) gave 2:2'-dipyridyl (94 g.) and 3:4'-dipyridyl (3.0 g. as picrate), alkylated 2:2'-dipyridyls (43 g.) and an oily residue (14 g.) not extracted with aqueous ferrous sulphate.

*Residue.* Mixed tripyridyls (100 g.) were isolated in the usual manner from the water soluble part of the residue and pure 2:2':2''-tripyridyl (24 g.) was prepared from the foregoing mixture by crystallisation from petroleum (b.p. 40-60°). 2:2':x''-Tripyridyl (m.p. 84-85°) was also identified in the oily residue after the crystallisation of its isomeride. The insoluble residue gave resins (183 g.) extractable by benzene while the insoluble portion gave combustible organic matter (362 g.).

#### *Co-ordination Compounds of Bivalent Metals.*

##### *Platinum Salts.*

*α-2:2'-Dipyridylplatinous chloride.* Potassium chloroplatinite (2.05 g.) and 2:2'-dipyridyl (0.78 g.) were heated in aqueous medium on the water-bath when an orange yellow microcrystalline platinous salt separated (1.35 g.) and a further quantity (0.5 g.) was obtained on evaporation. This complex salt was washed with water and alcohol and dried over sulphuric acid. (Found: Pt, 46.22; Cl, 16.19.  $C_{10}H_8N_2Cl_2Pt$  requires Pt, 46.23; Cl, 16.80 per cent.). *α-2:2'-Dipyridylplatinous chloride* was very sparingly soluble in water or organic solvents but dissolved in aqueous pyridine to a pale yellow solution.

*β-2:2'-Dipyridylplatinous chloride.* Potassium chloroplatinite (2.05 g.) dissolved in water (30 c.c.) was added with stirring to a solution of 2:2'-dipyridyl (2.3 g.) in dilute hydrochloric acid. The pale buff crystalline substance which separated was washed with cold water and alcohol. (Found: Pt, 30.32 per cent.). When this buff coloured salt was boiled with water it rapidly decomposed with the formation of *β-2:2'-dipyridylplatinous chloride* which filled the liquid

with a felted mass of pale yellow needles. (Found: Pt, 46.14; Cl, 16.41.  $C_{10}H_8N_2Cl_2$  Pt requires Pt, 46.23; Cl, 16.80 per cent.).

*Palladous Salt.*

*2:2'-Dipyridylpalladous chloride.* When warmed in aqueous medium 2:2'-dipyridyl and palladous chloride yielded a pale yellow crystalline palladous salt which was recrystallised from aqueous alcohol containing a little 2:2'-dipyridyl in slender pale yellow needles. (Found: Pd, 32.11.  $C_{10}H_8N_2Cl_2$  Pd requires Pd, 31.98 per cent.).

*Manganese Salts*  $[Mn\ 3dipy] X_2$ , where  $X=Cl, Br$  or  $I$ .

*Tris-2:2'-dipyridylmanganous chloride.* Manganese chloride (1 mol.) and 2:2'-dipyridyl (3 mol.) were heated together in aqueous medium until the diamine had dissolved. The yellow solution was filtered and cooled with stirring when the anhydrous manganese salt separated in small lemon yellow prisms. (Found: Cl, 12.50, Mn, 8.80.  $C_{30}H_{24}N_6Cl_2$  Mn requires Cl, 11.93; Mn, 9.24 per cent.). This complex chloride dissolved easily in water and by slowly crystallising a fairly dilute solution, tris-2:2'-dipyridylmanganous chloride *octahydrate* was obtained in large orange prisms. This hydrate speedily lost its combined water on exposure to the air, leaving a residue of the yellow anhydrous chloride. (Found: Cl, 9.80.  $C_{30}H_{40}O_8N_6Cl_2Mn$  requires Cl, 9.60; loss of  $H_2O$ , 18.8;  $8H_2O$  requires 19.5 per cent.).

*Tris-2:2'-dipyridylmanganous bromide heptahydrate* was precipitated when the foregoing chloride was dissolved in water and treated with a large excess of a concentrated solution of sodium bromide. It separated from hot water in flat pale orange yellow crystals which were air dried. (Found: Mn, 6.45, 7.08; Br, 19.65.  $C_{30}H_{38}O_7N_6Br_2Mn$  requires Mn, 6.79; Br, 19.76 per cent.). This hydrated bromide lost its water of crystallisation slowly on keeping and rapidly over sulphuric acid (loss of  $H_2O$ , 15.43;  $7H_2O$  requires 15.68 per cent.).

*Tris-2:2'-dipyridylmanganous iodide hexahydrate* when prepared in a similar manner to the foregoing bromide but using sodium or potassium iodide in place of sodium bromide, crystallised from water in flat light yellow crystals. (Found: Mn, 6.17; I, 28.49.  $C_{30}H_{36}O_6N_6I_2Mn$  requires Mn, 6.21; I, 28.68 per cent.).

This salt was the most stable of the three complex halides and only lost its combined water very slowly even in a vacuum over sulphuric acid (loss  $H_2O$ , 11.28;  $6H_2O$  requires 12.21 per cent.).

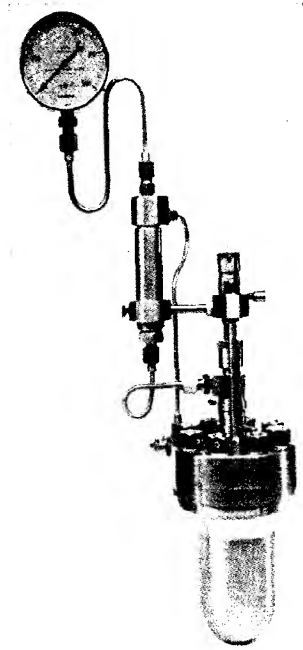
*Copper Salt.*

*Tris-2:2'-dipyridylcupric chloride hexahydrate* separated on evaporating an aqueous solution of cupric chloride (1 mol) and 2:2'-dipyridyl (3 mols.); it crystallised from water in pure blue tabular crystals and was air dried. (Found: Cl, 9.82.  $C_{30}H_{36}O_6N_6Cl_2Cu$  requires Cl, 9.97 per cent.).

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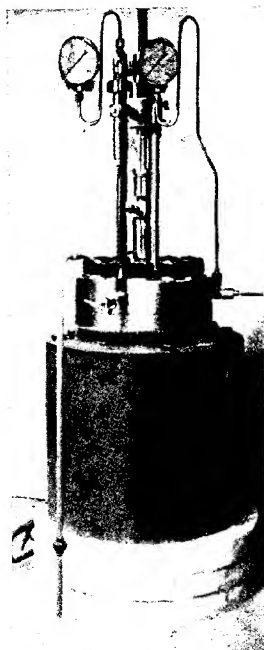
MORGAN AND BURSTALL

FIG. 1.



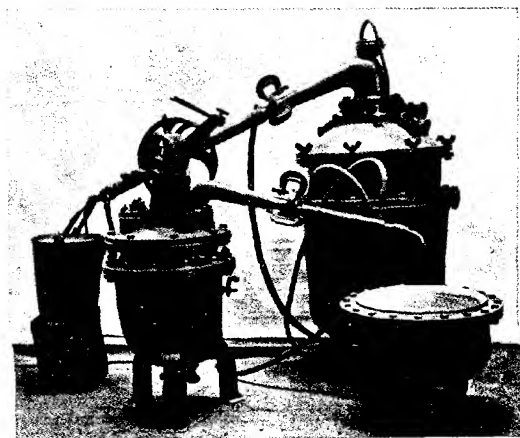
One litre autoclave constructed of Hadfield-Era (131) steel.

FIG. 2.



Eight litre gas-heated autoclave constructed of nickel-chromium-molybdenum steel.

FIG. 3.



Plant for steam-distilling dipyrityls and for concentrating dipyrityl hydrochlorides.



## On the Pyrolytic Condensation and Decomposition of Ethane in the Presence of Hydrogen.

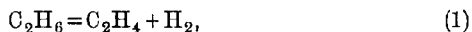
BY MORRIS W. TRAVERS.

It gives me much pleasure to make this small contribution to the volume of papers to be published in honour of my friend Professor Sir P. C. Rây. The volume will, I feel sure, bear evidence of his success in inspiring his students, and his student's students with enthusiasm for research in science.

This is a brief account of researches carried out in the University of Bristol with two of my students, Mr. L. E. Hockin, B.Sc., and Mr. T. J. P. Pearce, B.Sc. (*Proc. Roy. Soc.*, 1932, **136**, 1). It consists of a re-investigation of a problem which has passed through a great many hands, but which, regarded from a new standpoint, and studied by new methods, has led to results which call for revision of our ideas on a well worn subject. Most previous investigations have consisted in passing ethane through a hot tube, and examining the liquid and gaseous products. This is the method of the organic chemist. On the other hand the problem, and other similar problems have been studied by measuring the change of pressure which the gas undergoes when heated at constant volume, samples of the reaction mixture being analysed from time to time.

Some preliminary work had led us to the conclusion that most reactions involving organic compounds, when carried out at moderately high temperatures, were actually much more complex than the investigators thought, or wished them to be; and that many phenomena, such as so-called induction periods, and the like, could be accounted for on chemical grounds, when the problem came to be fully investigated. I decided therefore to adopt the principle of subjecting the problem to detailed investigation. This principle was not unsuccessfully applied in the researches which led to the discovery of the rare gases thirty years ago, and this was nearly the last piece of experimental work to which I was able to devote myself.

The method of investigation consisted in heating accurately measured quantities of the pure gases sealed up in silica glass tubes, for definite time periods and to definite temperatures, and subsequently making accurate analyses of the contents of each tube. Before each experiment a stem with a capillary constriction was sealed to the reaction tube; the tube was then exhausted, filled with hydrogen, and heated overnight. It was then again exhausted, cooled in liquid air, and the ethane, or other gas was condensed in it. Hydrogen, or other incondensable gas was then introduced, and the tube was sealed. After heating, the tube was quenched. It was then connected with an apparatus by means of which the point could be broken off and the contents removed. In the case of the experiments with ethane, the products were first of all ethylene and hydrogen resulting from the reversible reaction,



and then methane and benzene the products of condensation processes. These could be separated by cooling the tube with liquid air, pumping off the methane and hydrogen, and subsequently cooling the tube with solid carbon dioxide and alcohol, and pumping off the ethane and ethylene. The latter mixture was again condensed and fractionated to separate from it traces of hydrogen and methane. The benzene and other condensation products remained in the reaction tube.

The gases were analysed by special methods worked out in my laboratory (Broom, *J. Soc. Chem. Ind.*, 1928, **47**, 276r). The volumes of gas were measured dry, and only very small quantities of liquid reagents were used, so that a very high degree of accuracy was attainable.

Now our object was to investigate the manner in which the pyrolytic processes originated, and we were not otherwise interested in the final products, so we have regarded the quantity of carbon in the total condensate only as being a measure of the rate of reactions which lead to the formation of a product which is mainly benzene, through stages which are very rapid. Our conclusions seem to justify this assumption. The rate of formation of "condensate", determined as the difference between the carbon content of the gas originally present in the reaction tube, and the carbon content of the methane, ethane, and ethylene removed from the tube, is the factor with which we are mainly concerned.

In our first investigation we used pure ethane, which is easily obtained by treating zinc diethyl with water, condensing the gas in liquid air, pumping off incondensable gas, and finally evaporating from a bulb cooled to  $-80^{\circ}$ . The reaction tubes were filled to a concentration of 0.025 gram molecules of ethane per litre, so that the pressure at the reaction temperatures,  $590^{\circ}$  and  $610^{\circ}$  was about two atmospheres. However, even when all preliminary difficulties had been overcome, it was found practically impossible to analyse the results which we obtained, on account of the complications involved in the establishment of the ethane-ethylene-hydrogen equilibrium.

The simplest way to overcome this difficulty was to start with equilibrium mixtures of ethane, ethylene, and hydrogen, and this we did, making up various equilibrium mixtures, and introducing them into the reaction tubes in quantities such that the total quantity of ethane and ethylene amounted to 0.025 gram molecules of the two gases together. The ratio of the concentrations of the ethane and of the hydrogen could then be varied, the ethylene concentration diminishing and the ethane concentration increasing as the hydrogen concentration increased.

The value of the equilibrium constant  $\frac{P_{C_2H_4} \times P_{H_2}}{P_{C_2H_6}}$

(atmospheres) was found to be 0.0245 for  $590^{\circ}$  and 0.043 for  $610^{\circ}$ .

It simplifies description if all the data are set down in gram atoms of carbon or of hydrogen per litre.

In the graphs, Figures 1, 2, and 3, the abscissæ represent time in hours, and the ordinates quantities of products in gram atoms per litre,

A is the rate of change of hydrogen,

B is the rate of change of ethylene,

C is the rate of formation of total condensate,

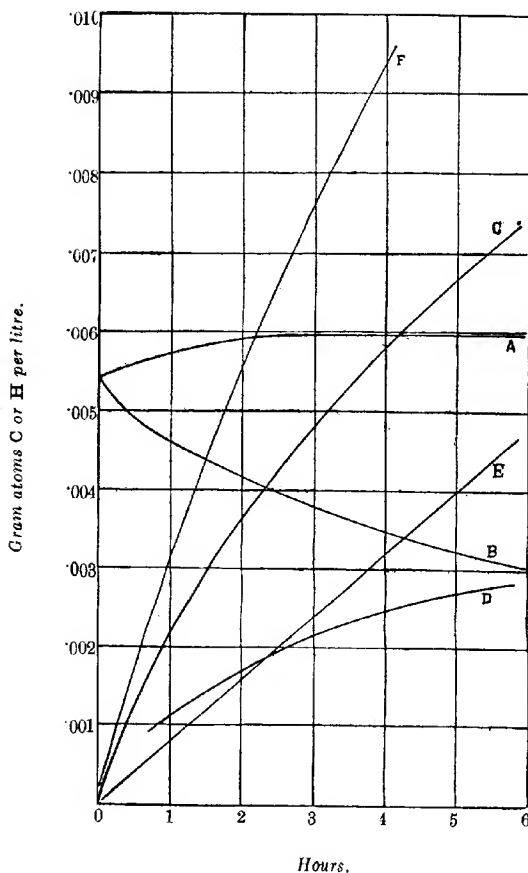
D is the rate of formation of condensate from ethane and ethylene,

E is the rate of formation of condensate from ethane alone,

F is the rate of formation of methane (Figure 1 only).



FIG. 1.



The experiments which we will now discuss were carried out at  $590^{\circ}$ .

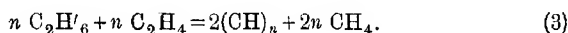
We are at first concerned only with that range of concentration of hydrogen which lies below 0.008 gram atoms per litre. Figure 1 refers to the equilibrium mixture containing (gram atoms per litre)  $C_2H_6$  0.04456,  $C_2H_4$  0.00544,  $H_2$  0.00544, that is equimolar quantities of ethylene and hydrogen. It will be noticed that the hydrogen increases slightly with time while the ethylene diminishes. Now, if we make the assumption that, within the limits of concentration of the hydrogen referred to above, hydrogen takes part only in the

reversible ethane, ethylene, hydrogen reaction, then it follows that  
(Increase in the hydrogen) + (Decrease in the ethylene)

$$= (\text{Ethylene converted into condensate}). \quad (2)$$

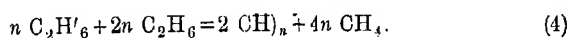
Later it will appear that we must assume that a reaction takes place between ethane and ethylene. If we now plot the sum of these two quantities against time, we obtain graph D; and if we subtract the values of condensate from ethylene (with ethane) from the values for the total condensate represented by graph C, we obtain the data which are plotted as graph E, which represent the quantities of condensate from ethane alone. The rate at which this process takes place is always represented by a straight line. Study of other equilibrium mixtures led to the conclusion that the formation of condensate from ethane, not involving ethylene is independent of the ethane concentration.

The rate of formation of methane is shown only in Figure 1, and only for the four hour period, and it is clear that methane is an important product, but it is not, as has been commonly supposed, the product of a reaction which is independent of the formation of condensate (benzene). Our investigation leads us to the conclusion that the various pyrogenic reactions which we have been studying are initiated by the activation of ethane, and that the rate of activation of the ethane is proportional to the square root of the hydrogen concentration. The activated ethane may react with ethylene giving rise to processes which are represented stoichiometrically by,



No mechanism is suggested by this equation. It is only written down to explain why though we measure the carbon appearing as condensate in terms of the ethylene which has disappeared, the latter is really a measure of that share of the rate of activation of ethane, which initiates the ethane-ethylene condensation process. We do not know whether it is the carbon of the ethane, or the carbon of the ethylene which appears as condensate or as methane.

Similarly, when ethane condenses without involving ethylene, we must have more methane produced, so that the stoichiometric relationship in the ethane-ethane condensation process may be represented by,



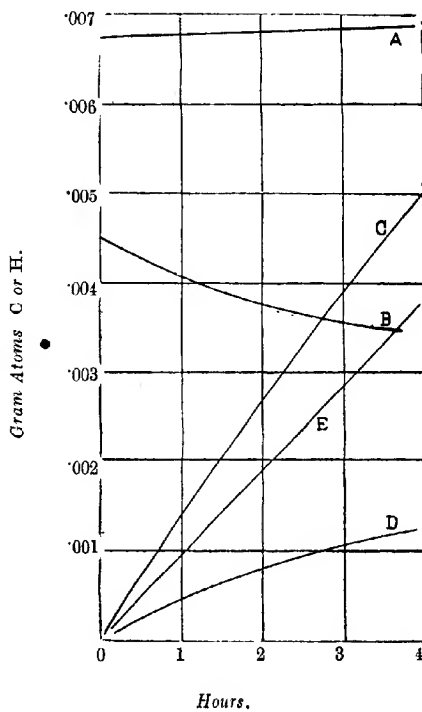
If these two relationships hold good, the ratio,

$$\frac{(\text{carbon in condensate})}{(\text{carbon in methane})},$$

should be unity in the case of the first process (3), and one-half in the case of the second (4). This is consistent with the analytical results.

To return to consider another equilibrium mixture. Figure 2 is related to a mixture with more ethylene and less hydrogen than that already considered. The mixture contains  $\text{C}_2\text{H}_6$  0.05175,  $\text{C}_2\text{H}_4$

FIG. 2.



0.00825,  $\text{H}_2$  0.00350. We find that as we proceed in this direction the linear graph E tends to approach the abscissa, and the case which we are now considering is that in which the amount of condensate exactly corresponds with the sum of the quantities,

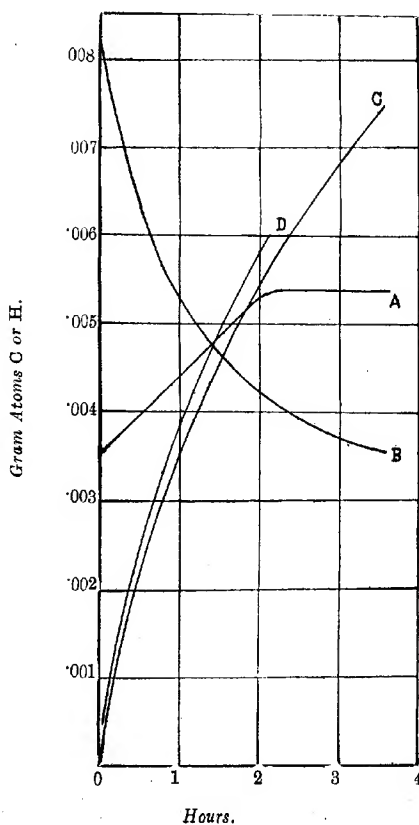
$$(\text{Decrease in ethylene}) + (\text{Increase in hydrogen}). \quad (5)$$

The graphs C and D are practically identical, and E vanishes. The conclusion is interesting; it is that below a certain hydrogen concentration, about 0.0038 g. atoms per litre, no condensate is formed by the ethane-ethane process, but only by the ethane-ethylene process. The latter is of course a strongly exothermic process, and the ethane-ethylene reaction is doubtless an example of an energy chain.

Figure 3 represents the changes in a mixture of initial composition,  $C_2H_6$  0.04550,  $C_2H_4$  0.00450,  $H_2$  0.00675. The changes are of the same character as in the case of the first mixture which we considered, the hydrogen increasing, and the ethylene decreasing.

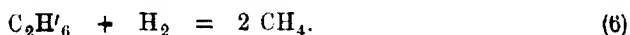
I shall now call attention to Figure 4. If we plot the slopes of the graphs which represent the rate of formation of condensate by

FIG. 3.



the ethane-ethane process (E), against the hydrogen concentration (g. atoms) as abscissæ, we obtain a graph  $a\ a'\ a''$ . The graph cuts the ordinate at  $a$ , and below the corresponding concentration of hydrogen (0.0038 g. atoms) no condensate is formed from ethane in absence of ethylene, or rather, all the activated ethane is taken up by the ethylene. A further proof of this is the fact that if we heat pure ethane, no condensate is formed till hydrogen and ethylene have been produced by the reversible reaction, and then as both the hydrogen and the ethylene concentration increases, the rate of formation of condensate is accelerated. The graph  $aa'a''$  shows a maximum at  $a'$ , and still the reactions, represented stoichiometrically by the equations 3 and 4, are the only ones which operate. However, above this concentration of hydrogen, ethylene no longer takes part in the condensation process to any appreciable extent.

A new reaction now sets in. While the rate of formation of total condensate is represented by a linear graph for equilibrium mixtures of hydrogen concentration above about 0.009 g. atoms of hydrogen, and no condensation is formed with disappearance of ethylene, methane is formed in excess of the quantity of the gas required by equation 4, and some hydrogen disappears. It is clear that we have now two processes operating. The one is the formation of condensate and methane according to equation 4, and the other is the formation of methane directly from ethane, according to the equation.



Calculating the quantity of methane corresponding to the quantity of condensate produced in any experiment, according to equation 4, and subtracting this from the total methane produced, we obtain, as difference, the quantity of methane corresponding to the reaction represented by equation 6. For any equilibrium mixture the rate of this process, like the rate of the process represented by equation 4, is linear with the time. The relationship between the rates of this process and the hydrogen content of the corresponding equilibrium mixtures is represented by the graph  $bb$ . It will be observed that as the rate of the process represented by equation 4 diminishes, that represented by equation 6 increases.

Equation 4 was written down to represent an activated ethane molecule ultimately yielding condensate equivalent to two gram

atoms of carbon, and equation 6 represents an activated ethane molecule yielding two molecules of methane. The sum of the quantities represented by points on the graphs *a* and *b*, for the same value of the hydrogen concentration, above about 0.009 g. atoms of hydrogen, that is above the concentration at which ethylene ceases to take part in the condensation process, should then represent the total rate of activation of ethane. The values so obtained are found to be proportional to the square root of the corresponding hydrogen concentrations, and the graph representing them, *cc*, has been calculated for all values to zero.

This fact appears to point to the conclusion that the three processes which we have considered,

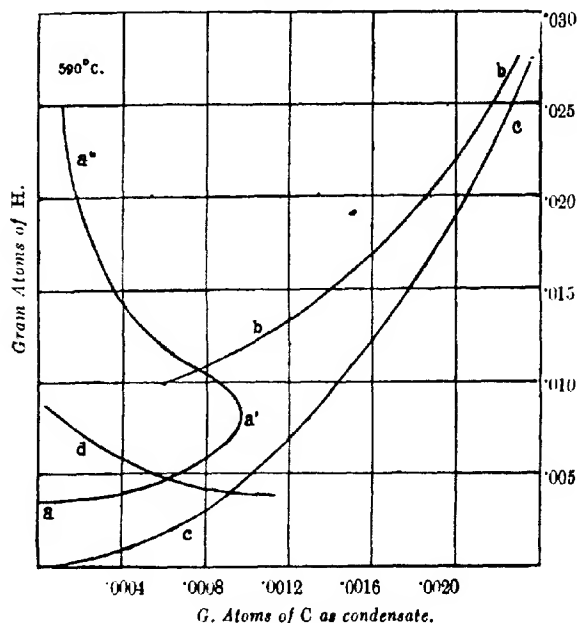
- (a) the formation of methane alone from ethane,
- (b) the formation of benzene and methane from ethane, alone,
- (c) the formation of benzene and methane from ethane and ethylene,

all originate in the activation of ethane, and by some mechanism in which the hydrogen is associated, possibly as atomic hydrogen. If this is the case, the activation of the ethane must be the slowest process, and there must follow a series of consecutive processes which are rapid. The apparent rate of each of the three processes should then be zero order, which is found to be the case with the two first mentioned above. However, it would not be likely to apply in the case of the process by which benzene and methane are formed from activated ethane and ethylene. This is a strongly exothermic process, and we should expect to find that the total amount of material transformed was in excess of the amount of material activated, through the operation of the principle of energy chain formation. That this is the case can be demonstrated in the following manner:

Reactions of this kind have commonly the appearance of being of a high order. Now if we determine the slopes of the curves representing the rates of formation of condensate (Graphs D) by the ethane-ethylene process, for short time intervals, and divide them by the fourth power of the ethylene concentration for the corresponding time period, we obtain a series of empirical constants for the different equilibrium mixtures. The values of these constants plotted against the corresponding hydrogen concentrations in Figure 4 gives the graph *d*, which represents the rate of the ethane-ethylene

condensation process increasing very rapidly as the ethylene concentration increases, becoming almost explosive at a hydrogen concentration of 0.0038 gram atoms, to the complete exclusion of the ethane-ethane condensation process. The total amount of change is now vastly in excess of the amount represented by a point on the graph *c*.

FIG. 4.



A series of experiments have also been carried out at 610°, and a graph corresponding to *c* has been calculated. Since in both cases the rate of formation of active ethane is proportional to the square root of the hydrogen the calculation of a critical increment is a simple matter. The value obtained is approximately 85,000 calories. This suggests the splitting of activated ethane into two methyl groups as the first stage in the process of formation of condensate. However, we will defer further speculation on this subject.

In conclusion I may say that this is but a brief account of a long and difficult investigation, and that I have been obliged to omit many facts which have been observed, and which confirm the conclusions which we have arrived at.

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## The Synthesis of Chromones.

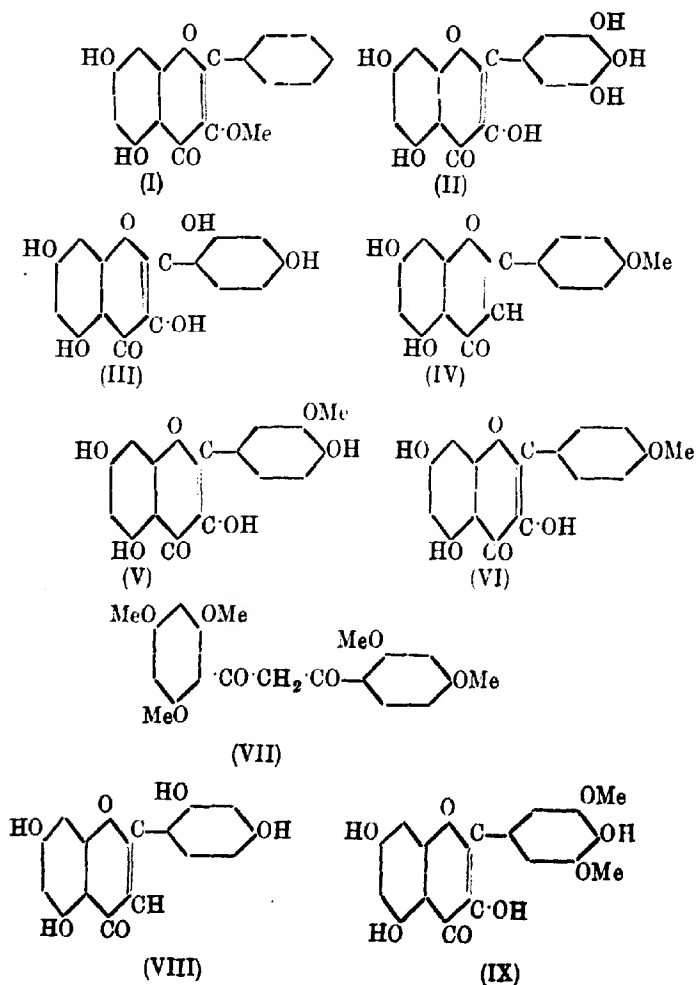
By KRISHNASAMI VENKATARAMAN.

Since the publication in 1918 of Perkin and Everest's "Natural Organic Colouring Matters," so much progress has been made in the synthesis of the important group of flavone pigments that a brief survey of the subject seems desirable.

Tahara (*Ber.*, 1892, **25**, 1302 ; see also Nagai, *ibid.*, 1287; Kostanecki and Rozycki, *Ber.*, 1901, **34**, 107) noticed that the prolonged action of acetic anhydride and sodium acetate on resacetophenone led to 3-acetyl-7-acetoxy-2-methylchromone, which could be hydrolysed to 7-hydroxy-2-methylchromone. It was not, however, till nearly 30 years later that the possibilities of the reaction for the synthesis of chromones and flavones were realised. Thus Crabtree and Robinson (*J. Chem. Soc.*, 1918, **113**, 859) used this method for the preparation of 7-hydroxy-3-benzyl-2-methylchromone and Allan and Robinson (*J. Chem. Soc.*, 1924, **125**, 2193) converted *o*-methoxyresacetophenone into 7-hydroxy-3-methoxy-2-methylchromone and 7-hydroxy-3-methoxyflavone by the action of acetic anhydride and benzoic anhydride respectively. The next advance was the application of the process to the synthesis of naturally occurring flavonols. By condensing *o*-methoxyphloracetophenone with benzoic anhydride and sodium benzoate, Kaff and Robinson (*J. Chem. Soc.*, 1925, **127**, 181) prepared a galangin monomethyl ether (I) which Testoni (*Gazzetta*, 1900, **30**, 327) had isolated from galanga root and to which the constitution shown had been assigned by Perkin and Allison (*J. Chem. Soc.*, 1902, **81**, 472). Similarly, the use of trimethylgallic anhydride and demethylation of the product yielded myricetin (II), the colouring matter of Chinese box-myrtle (*Myrica nagi*), and shortly afterwards, the synthesis on similar lines of datiscetin was carried out by the same authors. The interaction of *o*-methoxyphloracetophenone with 2:4-dimethoxybenzoic anhydride, followed by treatment with hydriodic acid, led to morin (III), the main colouring matter of old fustic (the wood of *Chlorophora tinctoria*, Gaudich) which, together with logwood, is the most important of the vegetable dyes and is still largely employed (Robinson and Venkataraman, *J. Chem. Soc.*, 1929, 61).



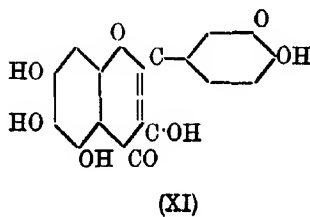
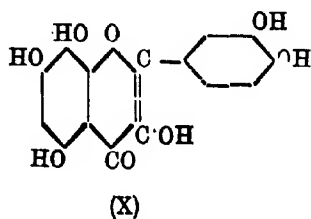
The previously known chalcone and ester methods of Kostanecki were limited in scope. The first sometimes led to the isomeric coumaranones and neither could be applied to the synthesis of partially methylated flavones such as acacetin (IV) or flavonols such as isorhamnetin (V) or kaempferide (VI). Difficulties also arose in particular cases; thus demethylation of 2:4:6:2':4'-pentamethoxybenzoylacetophenone (VII) resulted in a resin from which the expected 5:7:2':4'-tetrahydroxyflavone (VIII) could not be isolated (Bargellini, unpublished work); the formation of the flavanone required for the production of morin (III) did not proceed smoothly

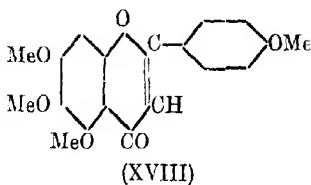
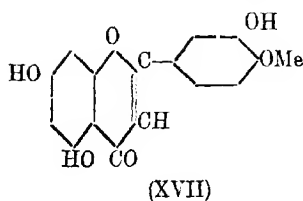
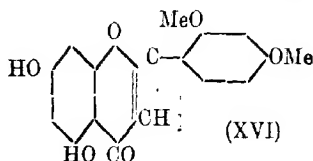
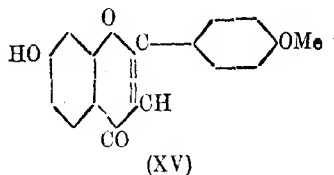
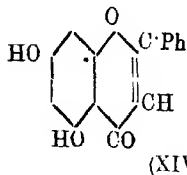
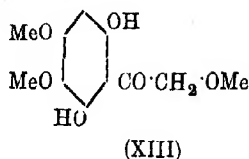
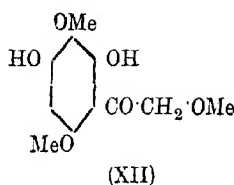


and only a minute amount of morin could be prepared (Kostanecki, Lampe and Tambor, *Ber.*, 1906, 39, 625); and finally, in the case of myricetin (II) the conversion of the flavanone into the isonitroso derivative was not feasible (Dean and Nierenstein, *J. Amer. Chem. Soc.*, 1925, 47, 1676). The Robinson reaction is of much wider application than the earlier methods of Kostanecki and some of the modifications may be briefly noticed.

The difficulty of preparing partially methylated flavonols was overcome by Heap and Robinson by the use of  $\omega$ -benzoyloxy in place of  $\omega$ -methoxyketones (*J. Chem. Soc.*, 1926, 129, 2336) and the synthesis of kaempferide (VI) and of isorhamnetin (V) was thus accomplished; in the latter case the anhydride of benzoylvanillic acid was employed. Similarly the action of *o*-benzylsyngic anhydride on  $\omega$ -benzoyloxyphloracetophenone, followed by successive hydrolysis with alkali and with alcoholic hydrochloric acid, gave myricetin-3':5'-dimethyl ether (IX) (Heap and Robinson, *J. Chem. Soc.*, 1929, 68); the substance, which has been named syringetin, is of interest on account of its relation to the anthocyanidin syringidin (malvidin), attention to whose wide distribution in nature has been called by Karrer and Widmer (*Helv. Chim. Acta*, 1927, 10, 5).

The new reaction was put to further use by Baker, Nodzu and Robinson (*J. Chem. Soc.*, 1929, 74) in the synthesis of gossypetin (X), the pigment of the flowers of the Indian cotton plant (*Gossypium herbaceum*), and of quercetagetin (XI), the pigment of the flowers of African marigold (*Tagetes patula*); quercetagetin has been isolated by Mahal and Venkatarman (unpublished) from the orange-yellow flowers of *Tagetes erecta* (Hindi and Bengalee, Genda). The veratroylation of the trimethoxyresacetophenone (XII) gave a hydroxy-pentamethoxyflavone, demethylation of which yielded gossypetin (X). The synthesis of quercetagetin (XI) proceeded from a second trimethoxydihydroxyacetophenone (XIII) by a similar series of reactions. The extension of the new method to the synthesis of flavones unsubstituted in the 3-position was carried out by Robinson





and Venkataraman (*J. Chem. Soc.*, 1926, **129**, 2344). The benzoylation of phloracetophenone and hydrolysis of the product led to chrysin (XIV), the pigment of poplar buds; anisoylation gave acacetin (XV), the colouring matter of the leaves of *Robinia pseud-acacia* (Linn.), and anisoylation of resacetophenone resulted in 7-hydroxy-4'-methoxy-flavone (XV) which was very probably identical with pratol, one of the flavone derivatives isolated by Power and Salway (*J. Chem. Soc.*, 1910, **97**, 231) from the common red clover (*Trifolium pratense*). Dunstan and Henry (*Phil. Trans.*, 1901, **194**, 515) assigned the structure of a 5:7:2':4'-tetrahydroxyflavone (VIII) to lotoflavin, the pigment obtained by hydrolysing the cyanogenetic glucoside lotusin, the active principle of the *Lotus arabicus* (Linn.). The substance (VIII) was synthesised by Robinson and Venkataraman (*J. Chem. Soc.*, 1929, 66) by demethylation of its dimethyl ether (XVI) and was found to exhibit little resemblance to lotoflavin (*cf.* Cullinane, Algar and Ryan, *Proc. Roy. Soc. Dublin*, 1928, **19**, 77).

A further example of the use of the Robinson reaction in the case of partially methylated flavones is the synthesis of diosmetin (XVII) (Lovecy, Robinson and Sugawara, *J. Chem. Soc.*, 1930, 817), which was obtained by hydrolysis and debenzoylation of the product of the action of *O*-benzylisovanillic anhydride on phloracetophenone.

An interesting transformation of a flavylum salt to a flavone has been achieved by Robinson and Schwarzenbach (*J. Chem. Soc.*, 1930, 822) who converted the pseudo-base of 4-amino-5:6:7:4'-tetramethoxyflavylum chloride into scutellarein tetramethyl ether (XVIII); this incidentally confirms the constitution of scutellarein, the pigment of the flowers and leaves of *Scutellaria altissima*, whose previous syntheses did not decide between alternative structures.

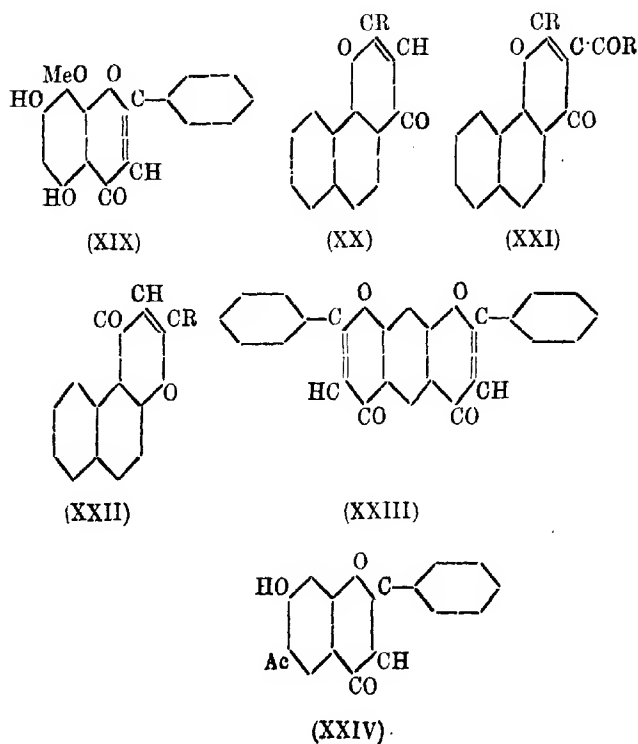
Two flavones, baicalein and wogonin, were isolated by Shibata, Iwata and Nakamura (*Acta Phytochim.*, 1923, 1, 105) and their constitution has been definitely proved by the work of Hattori (*Acta Phytochim.*, 1931, 5, 219). Wogonin is 5:7-dihydroxy-8-methoxyflavone (XIX); the benzoylation of 2-hydroxy-3:4-dimethoxy-6-ethoxyacetophenone, followed by dealkylation, led to 5:7:8-trihydroxyflavone, identical with the demethylation product of wogonin. Repeating Bargellini's work (*Gazzetta*, 1919, ii, 49, 47) on the action of hydriodic acid on 2:3:4:6-tetramethoxy-*o*-benzoylacetophenone, Hattori found that both 5:7:8-trihydroxyflavone and 5:6:7-trihydroxyflavone were formed; the latter was identical with baicalein.

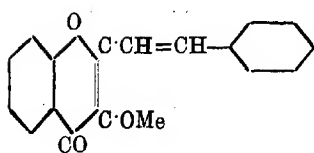
The chromone synthesis was applied to gallacetophenone by Venkataraman (*J. Chem. Soc.*, 1929, 2219); by benzoylation of the ketone and subsequent hydrolysis 7:8-dihydroxyflavone was obtained and was found to be comparable in its dyeing properties to luteolin which has two more hydroxyls. Attempting to prepare further flavones derived from pyrogallol it was found that the action of veratric and trimethylgallic anhydrides on gallacetophenone resulted in products difficult to crystallise. Recourse was therefore had to the ester method of Kostanecki and, by the demethylation of 2:3:4:3':4'-pentamethoxybenzoylacetophenone and 2:3:4:3':4':5'-hexamethoxybenzoylacetophenone, 7:8:3':4'-tetrahydroxyflavone and 7:8:3':4':5'-pentahydroxyflavone were prepared (Badhwar, Kang and Venkataraman, *J. Chem. Soc.*, 1932, 1107). For comparison with these in regard to dyeing properties and in order to facilitate the identification of new polyhydroxyflavones isolated from nature, 5:7:3':4':5'-

pentahydroxyflavone and 3 : 7 : 3' : 4' : 5'-pentahydroxyflavone were made by the Robinson method.

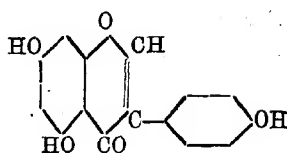
The process has been found applicable to the production of naphth- $\gamma$ -pyrones. When 2-acetyl-1-naphthol reacted with acid anhydrides, the 1:4- $\alpha$ -naphthapyrones (XX) were formed, but the simultaneous formation of the 3-acyl derivatives (XXI) was unavoidable and constituted a noteworthy feature of the condensation (Bhullar and Venkataraman, *J. Chem. Soc.*, 1931, 1165). With 1-acetyl-2-naphthol, the reaction proceeded normally, 1 : 4  $\beta$ -naphthapyrones (XXII) being formed (Menon and Venkataraman, *J. Chem. Soc.*, 1931, 2591); as in the benzene series *C*-acylation occurred only when acetic anhydride was used.

The preparation of dichromones by the action of acid anhydrides on 4:6-diacetylresorcinol has been described by Gulati and Venkataraman (*J. Chem. Soc.*, 1931, 2376). Heating the diketone with benzoic anhydride, a mixture of diflavone (XXIII) and 7-hydroxy-6-acetylflavone (XXIV) was obtained.





(XXV)



(XXVI)

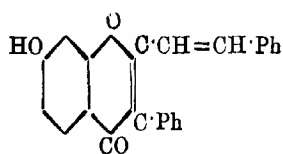
The possible occurrence of 2-styrylchromone derivatives in nature has been indicated by Robinson and Shinoda (*J. Chem. Soc.*, 1925, **127**, 1973); thus fukugetin,  $C_{17}H_{12}O_6$  (Perkin and Phipps, *J. Chem. Soc.*, 1904, **85**, 58) may be a tetrahydroxystyrylchromone and pratensol (Power and Salway, *loc. cit.*) may be a trihydroxystyrylchromone. The improbability of fukugetin being a styrylchromone has more recently been demonstrated by Shinoda (*J. Pharm. Soc. Japan*, 1926, No. 535, 736). As a contribution to the subject Robinson and Shinoda (*loc. cit.*) synthesised several 2-styryl-3-methoxychromones (XXV) by heating  $\omega$ -methoxyresacetophenone and  $\omega$ -methoxyphloracetophenone respectively with cinnamic (or substituted cinnamic) anhydride. The problem of preparing 2-styrylchromones unsubstituted in the 3-position has been investigated (Cheema, Gulati and Venkataraman, *J. Chem. Soc.*, 1932, 925) and it has been found that the Robinson reaction is inapplicable. The reactivity of the 2-methyl group in 2-methylchromones (Heilborn, Barnes and Morton, *J. Chem. Soc.*, 1923, **123**, 2565) was therefore utilised; the reaction was found to be much more general than these authors considered (*cf.* Chakravarti, *J. Indian Chem. Soc.*, 1931, **8**, 129, 619) and 2-styrylchromones derived from 2-methyl-1:4- $\alpha$ -naphthapyrone, 7:8-dimethoxy-2-methylchromone and 2-methylchromone were thus prepared.

The interaction of a phenol with a  $\beta$ -ketonic ester can obviously take one of two courses, a coumarin or a chromone being formed. The well known Pechmann method of preparing coumarins (Ber., 1883, **16**, 2119, *et seq*) consisted in the condensation of phenols with derivatives of ethyl acetoacetate in presence of sulphuric acid and, according to Simonis and his collaborators (Ber., 1914, **47**, 2229, *et seq*), the use of phosphorus pentoxide as condensing agent always led to chromones. Jacobson and Ghosh (*J. Chem. Soc.*, 1915, **107**, 424, 959, 1051) and Ghosh (*J. Chem. Soc.*, 1916, **109**, 105) claimed to have prepared numerous benzo- $\gamma$ -pyrones by condensing phenols with  $\beta$ -ketonic esters in presence of various condensing agents, *e.g.*,

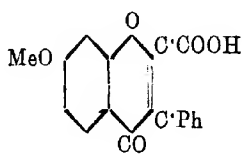
zinc chloride, sulphuric acid and hydrogen chloride. Baker and Robinson (*J. Chem. Soc.*, 1925, 127, 1981) and Baker (*ibid.*, 2349) synthesised the  $\gamma$ -pyrones of Ghosh by a method which excluded alternative structures and showed that the condensations of Ghosh led to  $\alpha$ -pyrones. It has also been found (Badhwar, Baker, Menon and Venkataraman, *J. Chem. Soc.*, 1931, 1541) that the condensation of  $\alpha$ -formylphenylacetonitrile and benzoyloxymethylenephylacetonitrile with phenols in presence of hydrogen chloride in ether solution led only to 3-phenylcoumarins and not to the isomeric isoflavones (3-phenylchromones). The work of Simonis has been submitted to fresh examination by Chakravarti (*loc. cit.* and *J. Indian Chem. Soc.*, 1931, 8, 407; 1932, 9, 25, 31), who has proved that the Simonis process is not of general application and that polyhydroxyphenols and  $\alpha$ -naphthol give coumarins even with phosphorus pentoxide (see also Robertson and others, *J. Chem. Soc.*, 1931, 1255, 1877, 2426; *Nature*, 1931, 28, 908). Chakravarti has made the interesting and important observation that only those phenols, which react with difficulty or do not react at all with  $\beta$ -ketonic esters in presence of sulphuric acid to form coumarins, yield chromones in presence of phosphorus pentoxide. The 2-methyl group in a 2-methylchromone is invariably reactive towards aldehydes and such styrylchromone formation can be employed to distinguish 2-methylchromones from the isomeric 4-methylcoumarins.

Finnemore (*Pharm. J.*, 1910, 31, 604) suggested that prunetol, obtained by demethylation of its monomethyl ether, prunetin, isolated from *Prunus* bark, may have an isoflavone structure (XXVI). Baker and Robinson (*J. Chem. Soc.*, 1926, 129, 2713) demonstrated the correctness of this suggestion and the identity of prunetol with genistein, which Perkin and Newbury (*J. Chem. Soc.*, 1899, 78, 830) had isolated from *Genista tinctoria* (Linn.). More recently, the synthesis of the substance has been accomplished by the same authors (*J. Chem. Soc.*, 1928, 3115) and the method may be indicated in general terms by the production of 7-hydroxy-2-styrylisoflavone (XXVII) as a result of the action of cinnamic anhydride on 2:4-dihydroxyphenylbenzylketone, oxidation of the methyl ether of (XXVII) to the isoflavone-2-carboxylic acid (XXVIII) and decarboxylation to 7-methoxyisoflavone (XXIX). A second general method for the synthesis of isoflavones has been developed by Baker, Pollard and Robinson (*J. Chem. Soc.*, 1929, 1468); the Hoesch reaction was carried out on the cyanhydrin of  $\omega$ -*m*-methoxy-

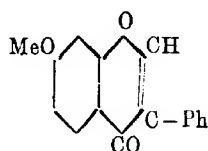
phenoxyacetophenone (XXX) and the 3-hydroxy-7-methoxyisoflavone (XXXI) thus formed was then dehydrated to 7-methoxyisoflavone. The process has been employed by Späth and Lederer (*Ber.*, 1930, 63, 743) for the synthesis of  $\psi$ -baptigenin (XXXII), which occurs in *Baptisia tinctoria* as the glucoside baptisin. Späth and Lederer (*loc. cit.*) have also described a second synthesis of the substance; the



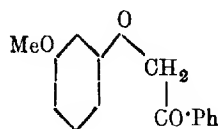
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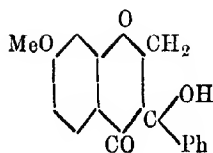
(XXVIII)



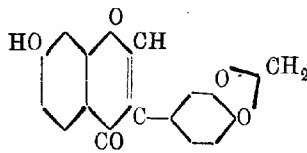
(XXIX)



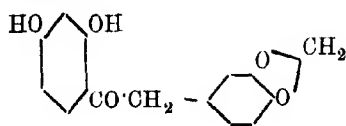
(XXX)



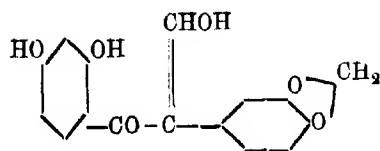
(XXXI)



(XXXII)



(XXXIII)



(XXXIV)



ketone  $\psi$ -baptigenetin (XXXIII) was condensed with ethyl formate and sodium and the product (XXXIV) was heated with alcohol and fuming hydrochloric acid. The formation of (XXXIV) is remarkable in view of the nonreactivity of 2-phenylacetyl-1-naphthol towards ethyl formate (Cheema and Venkataraman, *J. Chem. Soc.*, 1932, 918).

When an *o*-hydroxyketone interacts with an acid anhydride and the sodium salt of the acid, the possibilities are the formation of the acetate, of a coumarin, of a chromone and of a 3-acylated chromone. A comprehensive study of the reaction is in progress in this laboratory.

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**The Importance of Dialysis in Colloid Chemistry.  
Behaviour of Colloids towards Electrolytes  
and Non-electrolytes with Progress  
of Dialysis.**

BY B. N. DESAI.

On going through the rapidly increasing literature of colloid chemistry one comes across cases where different investigators trying the same experiments on the same colloid and with the same electrolytes have not been able to get similar results. No serious attempts seem to have been made till recently to find out the causes of this peculiar behaviour of colloids. It has been recognised that generally a colloid becomes more sensitive to electrolytes on subjecting it to dialysis. Dialysis has been utilised since the time of Graham for freeing a colloidal solution from the "impurities" necessarily introduced into it at the time of preparation, viz., the peptising agent and the other electrolytes formed as a result of double decomposition. The purpose of this article is to summarise some recent work on the behaviour of colloids with the progress of dialysis towards electrolytes and non-electrolytes.

Dhar and collaborators (*J. Phys. Chem.*, 1922, **26**, 70; 1924, **28**, 313; 1925, **29**, 453, 659; *Kolloid Z.*, 1924, **34**, 262; 1925, **36**, 129), from their extensive work with different colloids came to the conclusion that the dilution rule, viz., that the greater the concentration of a colloid the greater is the amount of an electrolyte necessary for coagulating it, is valid only for those colloids which are not capable of adsorbing appreciably from the coagulating electrolytes the ion carrying the same charge as the colloid. On the other hand, those colloids which appreciably adsorb the ion carrying the same charge as the colloid do not follow the general dilution rule when coagulated by *monovalent* coagulating ions. They have thus divided sols into two water-tight compartments. Dhar and Ghosh (*J. Phys. Chem.*, 1927, **31**, 187), have shown that a fairly pure sample of prussian blue sol is abnormal to the dilution rule when coagulated

by KCl and that the abnormality is increased by adding  $K_4Fe(CN)_6$  to the sol before coagulation. Weiser and Nicholas (*J. Phys. Chem.*, 1921, 25, 742), have, however, observed that the prussian blue sol behaved normally when coagulated by KCl. These results of Dhar and Ghosh and Weiser and Nicholas on the prussian blue sol, if considered critically indicate that the initial presence of different amounts of  $K_4Fe(CN)_6$  in their sols might be responsible for the different behaviour of the sol with KCl in the two cases. Desai (*Koll. Chem. Beih.*, 1928, 26, 384), has shown that colloidal solution of thorium hydroxide can be made to show normal or abnormal behaviour to the dilution rule when it is coagulated by electrolytes containing monovalent coagulating ion by subjecting the colloid to dialysis for different periods. These observations do show that it is erroneous to classify colloids into two divisions according to their behaviour towards the dilution rule, for a suitable adjustment of the amount of the peptising agent (by subjecting it to dialysis) seems to make a colloid behave normally or abnormally as in the case of colloidal thorium hydroxide.

According to the Schulze-Hardy law, equivalent amounts of different electrolytes with the same oppositely charged ion should coagulate a given sample of the colloid in the same time. Desai (*loc. cit.*) has observed that in the case of colloidal thorium hydroxide an impure sample of the sol (dialysed only for a small period and hence containing appreciable amounts of peptising agent) does not obey the Schulze-Hardy law. This abnormality, however, decreases with the progress of dialysis and a fairly pure sample of the sol (dialysed for a long period) does not show any deviation from the law. It is thus evident that colloidal thorium hydroxide can be made to behave either normally or abnormally to the Schulze-Hardy law by subjecting it to dialysis for different periods.

It has been shown (Desai, *Trans. Faraday Soc.*, 1928, 24, 181), that the rate of coagulation of colloidal thorium hydroxide in the sensitive range of electrolyte concentration is not a simple reaction as postulated by Smoluchowski (*Physikal. Z.*, 1916, 17, 557, 583; *Z. Phys. Chem.*, 1917, 92, 120), but that the nature of the coagulation process is auto-catalytic. The demonstration of the auto-catalytic nature of the coagulation reaction and the appearance of the S-shaped curves, however, depends on various factors, and of these the purity of the colloid is an important factor to be reckoned with. Patel and Desai (*Trans. Faraday Soc.*, 1930, 26, 128) have shown that the

coagulation velocity curves which are obtained with colloidal solution of thorium hydroxide dialysed for a sufficiently long period (and therefore containing only a very small amount of the peptising agent) are not S-shaped at any concentration of an electrolyte even for a concentrated sol.

It is a common belief that the stability of a colloid depends on the charge on its particles and that the greater the charge the greater is the stability. In the case of the gold sol prepared by Zsigmondy's nucleus method, it has been found that both charge and stability as determined by the flocculation value of KCl behave in a similar fashion on subjecting the colloid to dialysis (Freundlich, "*Colloid and Capillary Chemistry*," English Translation, 1926, p. 506; Nabar and Desai, *Nature*, 1931, **127**, 666). With colloidal arsenious sulphide Mukherjee and collaborators (*J. Indian Chem. Soc.*, 1927, **4**, 493), have observed that the stability is not so directly related to the charge as is generally believed to be. Measurements with colloidal ferric hydroxide have shown that although with the progress of dialysis the charge first increases and then decreases, the flocculation value with KCl shows a continuous decrease (Desai and Barve, *Nature*, 1931, **128**, 907). These results would also seem to show that there is no direct relation between charge and stability.

In a paper which will be published in due course, it is however shown that if proper consideration is given to changes in the adsorption of the similarly charged ions with the progress of dialysis when KCl is added, the initial decrease in the stability of colloidal ferric hydroxide in spite of an increase in the charge can be accounted for satisfactorily.

The results of viscosity measurements of colloids in presence of electrolytes are generally explained on the assumption that the viscosity is related to the charge on the colloid and that the smaller the charge on the colloid the greater will be its viscosity. The results of the viscosity measurements of colloids with the progress of dialysis are also explained on the basis of the same view. No simultaneous measurements of charge and viscosity have however been carried out to test the validity of the above view. Our preliminary results (unpublished) of the measurement of charge and viscosity of colloidal ferric hydroxide have shown that with the progress of dialysis, although the charge first increases and then decreases, the viscosity increases continuously. The explanation of this behaviour will be given in a subsequent paper.

Patel and Desai (*Kolloid Z.*, 1930, **51**, 318), have studied the behaviour of colloidal thorium hydroxide with the progress of dialysis towards non-electrolytes in the presence and absence of electrolytes. They have observed that with the progress of dialysis the sol is more and more easily sensitised by non-electrolytes and that a fairly pure sample of the sol (dialysed for a very long time) can be coagulated by non-electrolytes alone.

From the foregoing it would appear that a colloidal solution of any substance can probably show different behaviours towards electrolytes and non-electrolytes by subjecting it to dialysis for different periods. Dialysis removes along with other substances also the peptising agent and the initial presence of the latter in varying amounts can probably make a colloid show either a simple or complicated behaviour. It is, therefore, necessary that results of coagulation should always be accompanied with a statement about the purity of the sample of the colloid which has been investigated.

#### *Summary.*

Several cases of apparent abnormality of colloids in their behaviour towards electrolytes and non-electrolytes are considered. Experiments on colloids dialysed for different periods show that the apparent inconsistencies can be explained as being due to the initial presence in the colloids of varying amounts of the peptising electrolytes.

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## Studies in the Coagulation of Colloids. The Wall Effect.

By SHRIDHAR SARVOTTAM JOSHI AND V. LAKSHMI NARAYAN.

It has been observed before (Joshi and Narayan, *J. Indian Chem. Soc.*, 1930, 7, 883) that the autocoagulability of the manganese dioxide sol containing traces of alkali, increased appreciably when small amounts of such substances as filter and parchment paper, celluloid, animal charcoal, unglazed porcelain, all carefully cleaned before use, were introduced in the sol. Evidence showing that the walls of the containing vessel cannot be considered as but an inert component of the system was afforded by the observation that the characteristic precipitation of the manganese dioxide sol on the parchment paper during dialysis was very markedly reduced by applying a negative potential of about 200 volts to the dialysing septum. It was thought desirable therefore to investigate as to how far normal coagulations are susceptible to the influence of containing walls.

### EXPERIMENTAL.

The above possibility was examined in the coagulations of the colloid solutions of manganese dioxide, antimony sulphide, and positively charged ferric hydroxide. The first sol was prepared in the usual way from potassium permanganate solution and ammonia. It contained a trace of alkali which acted as a stabiliser. The colloid content was estimated by adding to a given volume of the sol a known amount of standard oxalic acid solution with some dilute sulphuric acid, and titrating the excess of oxalic acid by standard potassium permanganate solution. The antimony sulphide was prepared, and the colloid content estimated as described previously (*J. Indian Chem. Soc.*, 1931, 8, 11). The ferric hydroxide sol was made by adding ammonia to a solution containing about 6 grams of ferric chloride in 600 c.c. of water. The precipitate was separated by

decantation and washed several times with water till free from ammonia. It was then suspended in water and shaken with a small quantity of ferric chloride. A clear sol was obtained which was carefully filtered so as to separate completely the unpeptised ferric hydroxide. It was then dialysed till free from iron and chlorine. The colloid content of the sol was estimated by treating a known volume with concentrated hydrochloric acid at  $90^{\circ}$ . It was then reduced by adding a freshly prepared solution of stannous chloride. The excess of the latter was oxidised with minimum quantity of mercury bichloride. The ferrous iron was then estimated by titration with standard potassium dichromate solution using potassium ferricyanide as an indicator.

A convenient amount of the sol and the electrolyte solution having attained the thermostat temperature which was kept constant within  $0.5^{\circ}$ , 20 c.c. from each of the solutions were poured simultaneously in the coagulation vessel kept in the thermostat. After a definite time a certain amount of the mixture was centrifuged for 30 seconds in all cases, the number of revolutions per unit time being kept constant. 5 C.c. from the upper layers of the centrifuged mixture were then withdrawn and its colloid content estimated. This gives a measure of  $(a-x)$ , the uncoagulated part of the sol at a time  $t$ . In order to observe whether coagulation in glass vessels is subject to "wall reactivity," a fixed number of carefully cleaned, smooth glass beads of approximately uniform size were introduced in the system, the volume of the coagulating mixture before this, being the same as in the corresponding normal coagulation. A series of experiments was also carried out with a view to observe whether paraffinning the containing walls affected the corresponding rate of coagulation. In this series, the coagulating mixture always contained the same number of glass beads (which were smeared with a thin paraffin layer) as in the previous case, viz., 400. These three series of experiments were always carried out with the same sample of the sol and as far as possible under identical conditions. This method of increasing the wall area was preferred to the use of glass wool, chiefly because it is almost impossible to indicate even roughly the increase in area due to a given amount of glass wool. Moreover, it is exceedingly difficult to purify it thoroughly, and in experiments where the influence of paraffinating the containing walls and the wall material was investigated, its use is obviously impossible. The area of the containing walls in normal coagulations was approximately 60 sq.

cms. This increased by about 520 sq. cms. when glass beads were introduced in the coagulating mixture.

In the following results data for the colloid content of the sol for the concentration of the electrolyte solution, refer to a litre of the coagulating mixture.  $\beta$ , the Smoluchowski's constant and  $k$ , the bimolecular constant were calculated from the following equations respectively :

$$\beta = \frac{1}{t} \left[ \sqrt{\frac{n_0}{n_i}} - 1 \right]; \quad k = \frac{1}{t} \cdot \frac{x}{a(a-x)}$$

where the various symbols have their usual significance (*ibid.*). The data in Tables I and II indicate the course of coagulations of the manganese dioxide sol of different colloid contents and coagulator concentrations, each coagulation being studied with normal and increased wall area. Tables III and IV show respectively the effect of increasing the wall area on the coagulation of the same sol when the wall material was paraffined, and when a small amount of alkali was added to the coagulating sol. The progress of these coagulations is shown graphically in Fig. 1, and Fig. 2. Tables V and VI and curves in Fig. 3 show the 'wall effect' in the ferric hydroxide sol at two temperatures under different conditions mentioned above. Table VII and Fig. 4 refer to the coagulation of antimony sulphide sol.

FIG. 1.

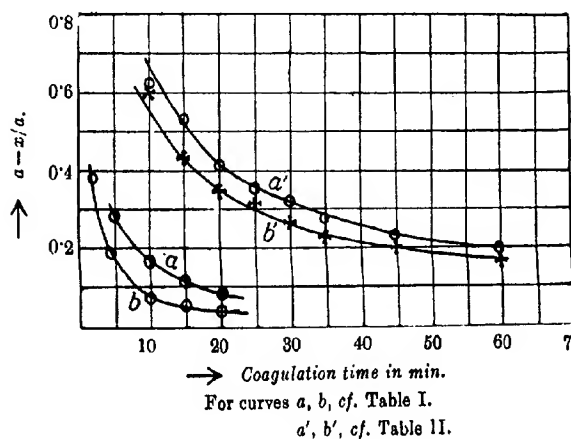




TABLE I (cf. curves *a*, *b*, Fig. 1).

Manganese dioxide sol.

Conc. of the sol = 0.304 g.  $\text{MnO}_2$  per litre.,, ,, ,, coagulator = 0.169 millimols of  $\text{BaCl}_2$  per litre.Temp., 28°.  $a = 2.33$  c.c. of oxalic acid soln.

A. Wall area (normal).					B. Wall area increased.				
Time in mins.	( $a-x$ ) in c.c. oxalic acid soln.	( $a-x$ )/ $a$ .	$\beta$ .	$k$ .	Time in mins.	( $a-x$ ) in c.c. oxalic acid soln.	( $a-x$ )/ $a$ .	$\beta$ .	$k$ .
5	0.64	0.275	0.18	0.23	2	0.88	0.378	0.13	0.35
10	0.40	0.171	0.14	0.21	4.5	0.43	0.185	0.30	0.42
15	0.28	0.118	0.13	0.21	10	0.16	0.069	0.28	0.58
20	0.18	0.077	0.13	0.26	15	0.11	0.047	0.24	0.58
					20	0.10	0.043	0.19	0.48

TABLE II (cf. curves  $a'$ ,  $b'$ , Fig. 1).

Manganese dioxide sol.

Conc. of the sol = 0.262 g.  $\text{MnO}_2$  per litre.,, ,, ,, coagulator = 18.18 millimols of  $\text{KCl}$  per litre.Temp., 28°.  $a = 6.02$  c.c. of oxalic acid soln.

A. Wall area, normal.					B. Wall area, increased.				
Time in mins.	( $a-x$ ) in c.c. oxalic acid soln.	$a-x/a$ .	$\beta$ .	$k$ .	( $a-x$ ) in c.c. oxalic acid soln.	$a-x/a$ .	$\beta$ .	$k$ .	
10	3.72	0.618	0.027	0.010	3.32	0.551	0.035	0.014	
15	3.19	0.53	0.025	0.008	2.6	0.432	0.035	0.015	
20	2.44	0.405	0.029	0.012	2.08	0.346	0.035	0.016	
25	2.11	0.351	0.028	0.012	1.82	0.302	0.033	0.015	
30	1.90	0.316	0.026	0.012	1.57	0.261	0.032	0.016	
35	1.61	0.267	0.027	0.013	1.31	0.218	0.032	0.017	
45	1.39	0.231	0.024	0.012	1.20	0.199	0.028	0.015	
60	1.20	0.20	0.02	0.011	0.94	0.156	0.026	0.015	

TABLE III (cf. curves *a*, *c*, fig. 2).

## Manganese dioxide sol.

Conc. of the sol. = 0.233 g.  $\text{MnO}_2$  per litre.

,, ,, ,, coagulator = 11.79 millimols of KCl per litre.

Temp., 28°.  $a = 5.39$  c.c. of oxalic acid.

A. Wall area, normal.					B. Wall area increased and paraffined.				
Time in mins.	( <i>a</i> - <i>x</i> ) in oxalic acid soln.	<i>a</i> - <i>x</i> / <i>a</i> .	$\beta$ .	<i>k</i> .	( <i>a</i> - <i>x</i> ) in oxalic acid soln.	<i>a</i> - <i>x</i> / <i>a</i> .	$\beta$ .	<i>k</i> .	
5	4.46	0.827	0.020	...	4.64	0.861	0.015	...	
10	2.14	0.397	0.060	0.028	2.45	0.455	0.048	0.022	
15	1.29	0.259	0.069	0.039	2.27	0.421	0.036	0.017	
25	0.84	0.156	0.061	0.040	1.34	0.249	0.040	0.022	
40	0.54	0.100	0.054	0.042	0.88	0.163	0.037	0.024	
60	0.31	0.058	0.053	0.051	0.53	0.093	0.036	0.028	

TABLE IV (cf. curves *a'*, *b'*, fig. 2).

## (Alkalinated) manganese dioxide sol.

Conc. of the sol. = 0.244 g.  $\text{MnO}_2$  per litre.

,, ,, ,, coagulator = 15.68 millimols of KCl per litre.

,, ,, ,, alkali = 1.08 millimols of KOH per litre.

Temp., 28.5°.  $a = 0.93$  c.c. of oxalic acid soln.

A. Wall area, normal.					B. Wall area increased.				
Time in mins.	( <i>a</i> - <i>x</i> ) in oxalic acid soln.	<i>a</i> - <i>x</i> / <i>a</i> .	$\beta$ .	<i>k</i> .	( <i>a</i> - <i>x</i> ) in oxalic acid soln.	<i>a</i> - <i>x</i> / <i>a</i> .	$\beta$ .	<i>k</i> .	
5	...	...	...	...	0.28	0.30	0.16	0.5	
10	0.86	0.925	0.004	0.0088	0.09	0.097	0.22	1.0	
15	...	...	...	...	0.06	0.065	0.20	1.0	
20	0.81	0.87	0.0036	0.008	0.03	0.0323	0.23	1.6	
25	0.80	0.86	0.0031	0.007	0.03	0.0323	0.20	1.3	
30	0.75	0.807	0.0038	0.0086	0.02	0.021	0.19	1.6	
40	0.65	0.697	0.0037	0.01	...	...	...	...	

TABLE V (cf. curves *a*, *b*, *c*, fig. 3).

Ferric hydroxide sol.

Conc. of the sol = 1.73 g.  $\text{Fe}_2\text{O}_3$  per litre.

,, ,, ,, coagulator = 37.1 millimols of KCl per litre.

Temp., 18°.  $a = 2.43$  c.c. of N/10-dichromate soln.

A. Wall area, normal.					B. Wall area, increased.				
Time in mins.	( $a-x$ ) in c.c. oxalic acid soln.	$a-x/a$ .	$\beta$ .	$k$ .	Time in mins.	( $a-x$ ) in c.c. oxalic acid soln.	$a-x/a$ .	$\beta$ .	$k$ .
10	2.2	0.906	0.005	0.0043	10	1.64	0.675	0.022	0.02
15	2.13	0.876	0.005	0.0039	15	1.32	0.543	0.024	0.023
20	1.99	0.82	0.005	0.0046	21	1.01	0.416	0.026	0.028
25	1.81	0.745	0.0064	0.0056	30	0.78	0.321	0.026	0.029
30	1.58	0.653	0.008	0.0074	41	0.63	0.259	0.024	0.029
35	1.17	0.482	0.013	0.013	49	0.52	0.214	0.024	0.031
40	0.75	0.309	0.02	0.023	60	0.39	0.161	0.026	0.036
45	0.63	0.259	0.022	0.026					
50	0.43	0.198	0.05	0.034					
65	0.31	0.128	0.03	0.043					

## C. Increased wall area, paraffined.

Time in mins.	( $a-x$ ) in c.c. oxalic acid soln.	$a-x/a$ .	$\beta$ .	$k$ .
10	2.34	0.963	0.002	...
20	2.24	0.923	0.002	0.0017
25	2.11	0.868	0.003	0.0025
30	1.97	0.811	0.004	0.003
5	1.72	0.708	0.005	...
40	1.26	0.519	0.0097	0.0096
45	1.00	0.412	0.012	...
60	0.54	0.222	0.019	0.024

TABLE VI (*cf.* curves  $a'$ ,  $c'$ , fig. 3).

Ferric hydroxide sol.

Conc. of the sol = 1.78 g.  $\text{Fe}_2\text{O}_3$  per litre.

Conc. of the coagulator = 37.1 millimols of KCl per litre.

Temp., 28°,  $a = 2.43$  c.c. of 0.1N-dichromate soln.

A. Wall area, normal.					B. Wall area, increased and paraffined.			
Time in mins.	( $a-x$ ) in c.c. oxalic acid soln.	$a-x/a$ .	$\beta$ .	$k$ .	( $a-x$ ) in c.c. oxalic acid soln.	$a-x/a$ .	$\beta$ .	$k$ .
10	1.24	0.51	0.03	0.04	2.16	0.889	0.006	0.005
15	1.12	0.461	0.025	0.032	1.95	0.802	0.0078	0.0068
20	0.84	0.346	0.024	0.039	1.80	0.741	0.008	0.0072
25	0.82	0.338	0.020	0.032	1.58	0.65	0.0096	0.0089
30	0.79	0.325	0.017	0.028	1.34	0.55	0.012	0.011
40	0.71	0.292	0.014	0.025	0.87	0.358	0.017	0.018
50	...	...	...	...	0.58	0.239	0.021	0.026

TABLE VII (*cf.* curves  $a$ ,  $b$ ,  $c$ , fig. 4).

Antimony sulphide sol.

Conc. of the sol = 0.672 g.  $\text{Sb}_2\text{S}_3$  per litre.

Conc. of the coagulator = 54.35 millimols of KCl per litre.

 $a = 0.5$  c.c. of dichromate soln.

A. Wall area, normal.					B. Wall area, increased.			
Time in mins.	( $a-x$ ) in c.c. oxalic acid soln.	$a-x/a$ .	$\beta$ .	$k$ .	( $a-x$ ) in c.c. oxalic acid soln.	$a-x/a$ .	$\beta$ .	$k$ .
10	0.46	0.92	0.0042	0.017	0.28	0.56	0.033	0.16
15	0.44	0.88	0.0044	0.018	0.25	0.50	0.028	0.13
25	0.40	0.80	0.0047	0.02	0.25	0.50	0.017	0.08
30	0.37	0.74	0.0054	0.023	0.23	0.46	0.016	0.09
40	0.29	0.58	0.0078	0.036	0.21	0.42	0.014	0.06
50	0.28	0.56	0.0067	0.031	0.19	0.38	0.012	0.065
60	0.20	0.40	0.0099	0.05	0.18	0.36	0.011	0.06
70	0.16	0.32	0.011	0.061				

TABLE VII—(continued).

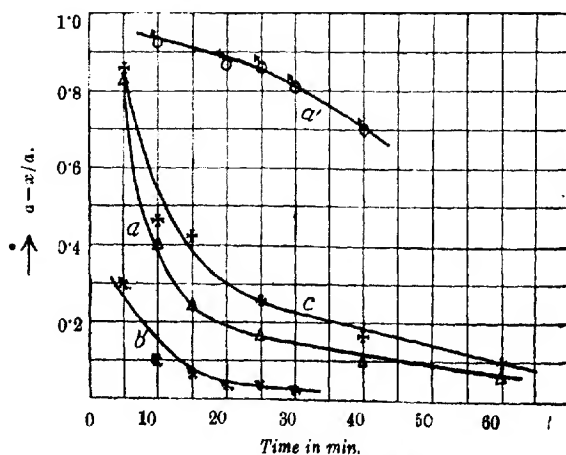
## C. Wall area, increased and paraffined.

Time in mins.	( $a-x$ ) in c.c. oxalic acid sol'n.	$a-x/a$ .	$\beta$ .	$k$ .
10	0.48	0.96	0.0021	0.0083
15	0.46	0.92	0.0028	0.012
25	0.2	0.84	0.0036	0.015
30	0.39	0.78	0.0044	0.019
40	0.33	0.66	0.0058	0.026
50	0.28	0.56	0.0067	0.03
60	0.24	0.48	0.0074	0.036
70	0.19	0.38	0.0089	0.047

## Discussion.

These results show that the rate of coagulation is markedly increased in all cases when the wall area of the coagulating system is increased by introducing glass beads. When, however, the same number of beads and the containing walls are paraffined, the coagulation is sensibly retarded in all cases, which shows that the wall effect depends upon the nature of the material in immediate contact with the coagulating sol. In the majority of cases both these aspects of the wall effect are maximum during the middle stage of the coagulation, and tend to diminish towards the end of the coagulation in all cases. The nature of the coagulating sol would also appear to be a determinant of the magnitude of the wall effect. This is illustrated by the results in Table IV and curves *a*, *b*, in Fig. 2 for the coagulation of alkaline manganese dioxide sol. In this case, it will be noticed that the effect of increasing the wall area on the rate of coagulation is strikingly greater than that in any other case studied here.

FIG. 2.



For curves *a*, *c* cf. Table III B  
*a'*, *b'*, cf. Table V.

It may be pointed out that the more important of the existing theories of the kinetics of coagulation (Smoluchowski, *Z. Phys. Chem.*, 1917, **92**, 129; Freundlich, *Colloid and Capillary Chemistry*, 1926, pp. 442-450), proceed on the tacit assumption that coagulation is a homogeneous reaction, that is, it results only from collisions amongst the colloid particles. The foregoing results on the wall effect reveal therefore the existence of a hitherto ignored factor, whose evaluation is necessary before a complete theory of coagulation can be built up. The essential heterogeneity of the coagulation process is implied in the conclusion of a number of workers (cf. Desai, *Trans. Faraday Soc.*, 1928, **24**, 191; also Freundlich, *loc. cit.*, pp. 434-447) that it is an autocatalytic reaction. This is based chiefly on the fact that the familiar equation for autocatalytic reactions is appreciably followed in a number of coagulations, the corresponding coagulation-time curves being S-shaped. This is usually explained by supposing that the coagulated particles accelerate the process by acting as nuclei for coagulation. This S-shape is noticeable in a number of coagulations (cf. Figs. 3 and 4).

FIG. 3.

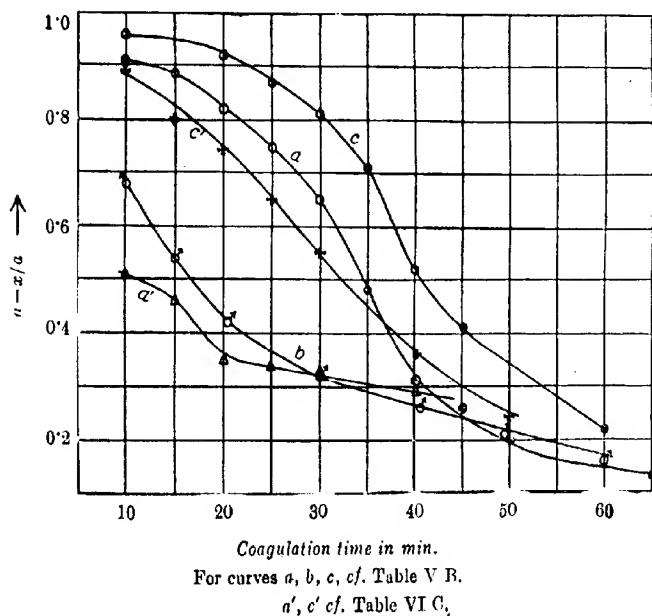
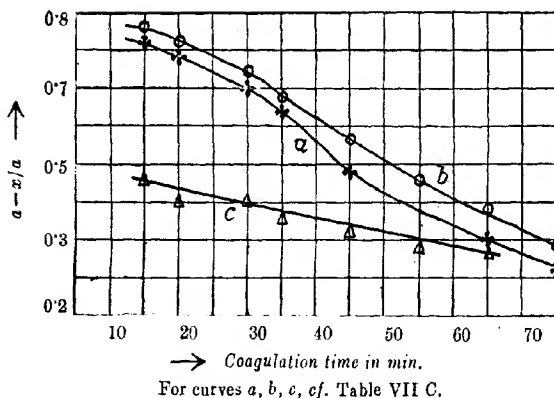


FIG. 4.



It is of great interest to observe that in coagulations produced in glass vessels, the S-shape is no longer present when the same coagulations are carried out in the presence of glass beads. This elimination of the S-shape is not seen when both the containing walls and the beads are paraffined. This difference of result illustrates clearly the specificity of the wall effect. It is also interesting to consider the values of  $\beta$  in relation to the wall effect. It will be seen that in all the coagulations which show an S-shape, in the corresponding coagulation-time curves (Figs. 3, 4),  $\beta$  tends to rise with the coagulation-time. This tendency does not appear to be sensibly reduced (in fact, pronouncedly increased in the majority of cases) during coagulations in paraffined containers. It is however very definitely reduced in all cases when the wall area is increased in glass vessels. It is of great interest to consider the results in Table V for the coagulation of ferric hydroxide sol. With normal (glass) wall area,  $\beta$  increases by nearly ten times within 50 minutes, when about 80 per cent. of the sol is coagulated. For the same coagulation under the same conditions, with the exception that the wall area is increased, during the above period,  $\beta$  remains practically constant, the percentage coagulation produced by this time being approximately the same as before. In terms of Smoluchowski's theory the latter is a 'rapid coagulation.' In agreement with the requirements of this theory, the bimolecular constant *increases* during coagulation, as is generally observed. A somewhat similar example

is afforded by the data in Table II for the coagulation of manganese dioxide. It will be seen that in the normal coagulation during an appreciable part of the change,  $\beta$  is almost constant. The same obtains when the wall area is increased, the values of  $\beta$  being uniformly greater. The same remark applies to the  $k$  values for the two series of coagulations, which would thus appear to be intermediate between 'rapid' and 'slow' coagulation. In the coagulation of the antimony sulphide sol, considering the variation of  $\beta$  and  $k$  with time (cf. Table VII, and the curves in Fig. 4), it is seen that with normal glass surface (as also with paraffined walls) the change is autocatalytic. This characteristic is eliminated (cf. Curve b, Fig. 4 and Table VII B) when glass beads are introduced; moreover, the resultant coagulation in this case belongs to the 'slow' region of coagulation. In the light of these results, it is not without interest to enquire whether the increase in the rate of coagulation, under wall effect alone, can convert a 'slow' into a 'rapid' coagulation. This would appear to be unlikely since the main characteristic of the 'rapid' coagulation is that the particles are more or less completely discharged, whereas in slow coagulations initially, they are presumably appreciably charged. It follows, therefore, that the question whether a given coagulation is 'rapid,' is not determined by the magnitude of the rate of its coagulation, which is seen to be variable under wall effect, as possibly under the operation of other factors such as viscosity, a higher temperature, etc.

These results show, therefore, that 'autocatalysis' can not be considered as a general characteristic of coagulation as has been supposed by some workers in discussing the limitations of the applicability of Smoluchowski's theory. This agrees with a deduction made previously from independent data (cf. *J. Indian Chem. Soc.*, 1931, 8, 342). Autocatalysis being but a secondary process which adds on to the main course of coagulation under certain conditions, its elimination is necessary, before data for a given coagulation can be employed for examining the applicability of Smoluchowski's theory. To this end, as shown by results in Table V discussed above, use of wall material in divided form, would appear to be a simple means.

A further theoretical treatment of the mechanism of the 'wall effect' will be published in a later communication. Work is in progress in order to study this phenomenon in other coagulating sols and under different conditions.



*Summary.*

Results are given for the coagulation of the colloid solutions of manganese dioxide, antimony sulphide and ferric hydroxide by different coagulators with (a) normal wall area in glass vessels, (b) when this area was increased about four times by introducing glass beads, and (c) when the containing walls and the beads were paraffinned. A number of these coagulations were found to be autocatalytic, as judged from rise in  $\beta$  with time and the corresponding coagulation-time curves being S-shaped. The rate of coagulation was markedly increased and autocatalysis diminished under (b). The opposite was observed under (c). Both these types of the wall effect diminish during the last stages of coagulation. In general the course of coagulation becomes simplified under (b) and is assignable as belonging to the region of 'slow' or the 'rapid' coagulation as contemplated in Smoluchowski's theory. It is considered that 'autocatalysis' is not fundamental to coagulation, in general.

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## **The Utilisation of Methane.**

By T. S. WHEELER.

### *Introduction.*

The utilisation of the enormous quantities of methane now wasted as coke-oven and as natural gas is one of the pressing problems of modern chemical technologists. There are described below the published results of a series of co-ordinated researches made in an endeavour to solve this problem. These results have so far been given only in a disjointed manner mostly in British and other patents and they are here summarised and co-ordinated.

In chemical reactions, which it is hoped to work on a large scale, it is essential that the raw materials be available in quantity. To obtain new results with such materials it is necessary that they be treated in new fashion, that is, that a new technique be involved. The technique underlying the researches to be described is one which has not yet been much exploited by the chemical industry. It may be referred to as the high temperature-high space velocity method of working; that is to say the substances undergoing reaction are heated at high temperatures for very short periods of time; (usually less than 0.01 minute in these researches).

This method of working has a two-fold advantage in that (i) a small plant can be made to give a high output and (ii) should explosion occur in the reaction chamber only a small quantity of material is involved.

The reactions studied were:

- (1) the production of hydrogen cyanide from methane,
- (2) the production of carbon disulphide from methane,
- (3) the production of aromatic hydrocarbons from methane,
- (4) the chlorination of methane.

As subsidiary researches there arose from (4)

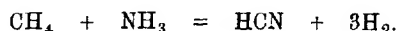
- (5) the chlorination of propane, methyl chloride, benzene, and toluene in the gaseous phase.

*The Production of Hydrogen Cyanide from Methane.*

Methane has, compared with its elements, a low energy content. Hence in order to obtain other products from methane, it must be treated at high temperatures to form substances relatively stable at these temperatures, or alternatively, it must be made to react with substances of high energy content such as chlorine.

An examination of substances tending to be stable at high temperatures, closely related to methane, and of industrial importance revealed two outstanding products, hydrogen cyanide and carbon disulphide. Experiments were therefore begun on the production of hydrogen cyanide from methane.

In commencing a series of experiments on a problem of this kind, it is always advisable to proceed from the known to the unknown. Accordingly, the known reaction between nitrogen and methane in the electric arc, which produces hydrogen cyanide, was first examined. The yields measured in output per unit of energy were poor, so ammonia was substituted for nitrogen as it is chemically more labile. The improvement obtained was not great. It was then sought by preheating the mixture of methane and ammonia passing to the arc, to replace portion of the electrical energy used by the cheaper thermal energy, in other words to take the heating load off the arc (I. C. I. Ltd. and Wheeler, B. P. 325, 860). The yields when the preheating furnace was at 1000° increased so rapidly that it became clear that during the heating, interaction between ammonia and methane was taking place, according to the equation



Since thermal energy is cheaper than electrical energy, a study was made of the conditions under which methane and ammonia react to form hydrogen cyanide. Application of Nernst's approximate equation and of Lewis' free energy method showed that at about 1350° good conversions to hydrogen cyanide should be obtained. Eventually, as a result of a series of experiments (I.C.I. Ltd., Wheeler, McAuly, Fletcher and Mills, B. P. 335, 585, 335, 947; I.C.I. Ltd., Wheeler and Fletcher, B.P. 349, 958) it was established that with an inner wall temperature of the reaction chamber of about 1400° the process could be carried out so as to give almost complete conversion. The time of reaction must be short (0.01 min.). The material of the reaction chamber should be silica or sillimanite as

these substances do not catalyse the decomposition of ammonia into its elements. Metallic oxides which catalyse the decomposition must naturally be avoided, and on this account it is essential that the silica or sillimanite used should be free from iron oxide.

It is also advisable that the proportion of surface to volume in the reaction chamber should be as low as is possible consistent with the input of the necessary quantity of heat. This may be referred to the fact that the formation of hydrogen cyanide is apparently a homogeneous reaction, that is, it occurs in the gaseous phase, whereas the homogeneous decomposition of ammonia at these temperatures is very slow, this decomposition being chiefly a heterogeneous or surface reaction.

On this account a smooth surface is to be preferred to a rough one so that some form of internal glazing is desirable.

The reaction involved is strongly endothermic, and in order to heat up the gases and bring about interaction, considerable quantities of heat have to be passed from the flues through the walls of the chamber into the gas. The quantity is limited by the temperature gradient through the walls; this can be increased by making the walls thin and the flue temperature high. But there are practical limits to these desiderata, and actually in order that the necessary quantity of heat may enter, the chamber must have a certain minimum surface-volume ratio.

A great deal of physical engineering calculations is necessary to determine the maximum permissible width for these reaction chambers. The heat transfer possible through the walls of the chamber allowing for the resistance of the wall and the gas films adhering to both sides is readily calculated. While, however, part of the heat is transmitted to the reaction gases by convection, the greater portion is transmitted by radiation. The calculation of the quantity of heat transferred in this way is difficult.

As a result of calculation it is found that a suitable chamber is long and deep in proportion to its width. It can, for example, be internally 2 m. long, 1 m. high, and 5 cm. wide. A number of units could in practice be built side by side with flues interposed so as to form an apparatus of sandwich construction. With a chamber of this type of sillimanite the decomposition of ammonia is not excessive. This was proved by experiments with a chamber 1 m. long, 5 cm. high, and 5 cm. wide.

Any tendency of methane or hydrogen cyanide to decomposition in a narrow chamber is reduced in presence of a slight excess of ammonia above that required for complete conversion of the methane. The presence of hydrogen or of water vapour is also effective in this respect.

When it was found that the initial presence of hydrogen had a beneficial effect, it became possible to use coke-oven gas directly, and to convert methane and the other hydrocarbons present in it into hydrogen cyanide and hydrogen. This is a point of practical importance.

As an example of the laboratory application of the process, an experiment may be quoted in which the reaction tube consisted of an unpacked clear silica tube of diameter 2 cm. heated in an electric furnace 30 cm. long at 1490°. The inlet gas contained 55% by volume of ammonia and 45% of methane. The time of heating was 0.01 min., and under such conditions it was found that carbon decomposition was practically nil, while the exit gas had only slight traces of suspended carbon.

The gas was cooled and passed through a bag filter to remove this carbon. It was discovered that electrostatic precipitation led to decomposition of hydrogen cyanide. The latter was recovered by leading the gas through 20% sodium hydroxide solution; ammonia was washed out with sulphuric acid. It was found that 93% of the methane applied was converted to hydrogen cyanide which comprised 21.2% of the exit gas. This gas after washing consisted mainly of hydrogen. Similar results were obtained when coke-oven gas was employed.

The solution of sodium cyanide can be evaporated to dryness under reduced pressure without loss of cyanide if the mass is kept slightly alkaline throughout.

At present sodium cyanide, which finds a ready sale principally for gold extraction, is manufactured by the action of ammonia on a mixture of molten sodium and carbon. The reaction is smooth and rapid because two high-energy bodies, sodium and carbon, are employed. The energy used in the production of sodium is electrical, so that it is economically important if the energy necessary to produce sodium cyanide can be obtained thermally, as in the proposed process. On the other hand the application of thermal energy at high temperature involves great wear and tear of plant, and it is a matter for large scale

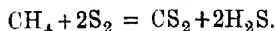
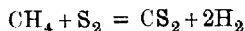
tests as to whether this rapid deterioration is balanced economically by the high cost of electrical energy.

In addition to the main work on the production of hydrogen cyanide, experiments were also carried out on its utilisation. It was found that in the production of ethylene cyanide from ethylene chloride and sodium cyanide, ethylene cyanide itself could replace alcohol as a solvent for the reaction (I.C.I. Ltd., and Wheeler, B. P. 333, 989). It is often useful in preparative work to employ an excess of the desired product as a solvent.

Again ethyl lactate can be prepared in one operation from acetaldehyde, hydrogen cyanide and alcohol; a process of alcoholysis was devised for converting the ethyl lactate (I. C. I. Ltd., Hurtleley and Wheeler, B. P. 346, 486) into butyl lactate which is of value as a solvent for lacquers.

#### *The Production of Carbon Disulphide from Methane.*

The production of carbon disulphide by the interaction of methane, either pure or as coke-oven gas, with sulphur or hydrogen sulphide was investigated using a technique similar to that described above (I.C.I. Ltd., Fletcher, Wheeler and McAulay, B. P. 331, 734). With a heating period of 0.005 minute at 1400°, about 50 % of the methane and sulphur applied in equivalent proportions was converted into carbon disulphide according to the equations,



It is impossible to obtain higher conversions owing to the equilibrium which is set up. Little direct decomposition to carbon occurs under the conditions of the experiment.

This process has an advantage over the normal process using carbon and sulphur, because coke-oven gas is more readily handled than carbon, but it is at a disadvantage in that higher temperatures are required for the reactions.

Carbon disulphide was recovered from the exit gas by washing with a suitable solvent such as creosote oil. The investigation of some of the problems involved in this recovery led to advance being made in the theory of boiling point rules (Wheeler, *Phil. Mag.*, 1931, 11, 441; 1931, 12, 685).

*The Production of Aromatic Hydrocarbons.*

It is known that by heating methane, ethane, ethylene, etc., at high temperatures, aromatic hydrocarbons can be obtained. The high temperature-high space velocity technique which was at the basis of the researches described was applied to this "pyrolysis" reaction (I.C.I. Ltd., and Wheeler, B. P. 324, 939; I.C.I. Ltd., Wheeler and Mc Aulay, B. P. 332, 998; I.C.I. Ltd., Wheeler, McAulay and Francis, B. P. 342, 319, 342, 359; I. C. I. Ltd., Wheeler and Francis, B. P. 351, 994). Using tubes a few millimetres in diameter, it was found possible to work at very high space velocities. Thus with a tube 3 mm. in diameter, 50 % of the applied ethylene was converted into oil when heated at 1100° for 1/6400 min. With larger tubes the reaction is not so rapid as the input of the necessary heat is not so readily accomplished. The time of heating must then be extended to 0.005 min. When the gas consists of a mixture of hydrocarbons, *e. g.*, the first four aliphatic hydrocarbons, it is best to carry out the process in stages beginning at 1200°, and increasing to 1240°, so that higher and then the lower hydrocarbons are attacked. The formation of carbon is reduced in this way.

The subject of the decomposition of methane was also considered from the theoretical aspect (Wheeler, *Fuel*, 1931, 10, 175; *Rec. trav. Chim.*, 1931, 50, 874; 1932, 51, 342.)

*Exothermic Reactions at High Temperature.*

The work so far described involved the application of the high space velocity-high temperature technique to endothermic reactions. Here the reduction of the time of heating was limited by the fact that it was necessary to convey heat to the reacting gas. It became of interest to determine what space velocities could be used with exothermic reactions at high temperatures (Binnie and Wheeler, *J. Soc. Chem. Ind.*, 1932, 50, 418T; B.P. 353, 913).

The following reactions were examined in preliminary experiments:

- (a) the removal of oxygen from air by hydrogen, the hydrogen being in such proportion that the exit gas is suitable for ammonia synthesis;
- (b) the production of hydrogen chloride from hydrogen and chlorine;
- (c) the interaction of hydrogen and chlorine in presence of methane.

The results obtained were remarkable. It was found that when a mixture of 5 volumes of air and 14 volumes of hydrogen was passed through a silica tube 0.25 cm. diameter at 1200°, all the oxygen was

removed as water even when the heating period was reduced to one-millionth of a minute. This time of heating corresponded to a rate of flow of gas of 500 litres per minute.

With hydrogen and chlorine external heating was unnecessary. A Y-shaped burner was made of silica tubing of bore 0.25 cm. Initially the junction was heated, and hydrogen was admitted to one limb, and chlorine to the other. With this burner, 21.6 litres of chlorine could be combined with 21.6 litres of hydrogen per minute corresponding to a production of 2.3 tons of 28% hydrochloric acid per week. It was also found possible to burn hydrogen and chlorine under water and obtain hydrochloric acid directly.

When methane is introduced into the zone of combination of hydrogen and chlorine, the energy of formation of hydrogen chloride becomes available to energise the transformation of methane to acetylene, which is a strongly exothermic reaction. Up to 27% of the methane applied can be converted into acetylene in this way. The use of the energy of a strongly exothermic reaction to induce endothermic reactions offers possibilities in industrial practice.

#### *The Chlorination of Methane at High Temperatures.*

In addition to these general experiments on exothermic reactions at high temperatures, a careful study was also made of the chlorination of methane at high temperatures (Mason and Wheeler, *J. Chem. Soc.*, 1931, 2282; B. P. 342, 329). At 1400° practically complete reaction occurred with a heating period of 1/30,800 minute. There was, however, considerable decomposition of methane to carbon and hydrogen. At 900° with excess of methane and heating periods of the order of 1/10,000 min. the method is suitable for the production of methyl chloride.

#### *The Chlorination of Propane, Methyl Chloride, Benzene and Toluene in the Gaseous Phase.*

The satisfactory results obtained with methane led to a study being made of the chlorination of propane, methyl chloride, benzene and toluene in the gaseous phase, using high temperatures and high space velocities (Mason and Wheeler, *loc. cit.*; Mason, Smale, Thomson and Wheeler, *J. Chem. Soc.*, 1931, 3150).

At 700°, and with a time of heating of 1/1000 min. the yield of propyl chlorides reached 86%. At 600° and with a space



velocity of  $1,660 \text{ mins.}^{-1}$  (reciprocal of time of heating) the yield of methylene chloride was about 96%.

The experiments on the action of chlorine on benzene and toluene yielded interesting results. It was found that at about  $500^{\circ}$ , with a period of heating of about  $1/500 \text{ min.}$ , chlorine reacts completely with excess of toluene to form benzyl and benzal chlorides. Unless iodine or other carrier be present little chlorine enters the nucleus. Chlorine also reacts similarly with excess of benzene at above  $450^{\circ}$  with a heating period of  $0.02 \text{ min.}$  to yield mono- and dichlorobenzenes with little or no trichlorobenzene. Addition of a carrier is unnecessary. This appears to be the first time that benzene has been substituted in the nucleus without a carrier.

*Summary.*

An account is given of the published results of a series of technical researches involving a new high space velocity-high temperature technique carried out with the object of examining possible methods of utilising methane.

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## Note on the Thermodynamic Functions of Radiation.

By F. G. DONNAN.

By radiation is meant *full* radiation in thermal equilibrium at a given temperature  $T$ . As is well known, the energy and entropy of the radiation are functions of the temperature and the volume, being given by the equations  $U = aT^4v$ ,  $S = \frac{4}{3}aT^3v$ , where  $U$ =energy,  $S$ =entropy,  $v$ =volume, and  $a$ =the Stefan constant.\*

Let us denote by  $A$  the monothermic work function, defined by the equation  $A = U - TS$  (*Helmholtzian* free energy function). Then it follows from the above results that  $A = -\frac{1}{3}aT^4v$ . Thus for two monothermic states having volumes  $v$  and  $v + \Delta v$  respectively, and the same temperature  $T$ , it is easily seen that  $(-\Delta A)_{v \rightarrow v + \Delta v} = \frac{1}{3}aT^4\Delta v$ . Now  $-\Delta A$  means the (maximum) work yielded by the radiation in the isothermal reversible expansion  $v \rightarrow v + \Delta v$ . Hence  $-\Delta A = p\Delta v$ , where  $p$  is the (Maxwellian) radiation pressure. It follows that  $p\Delta v = \frac{1}{3}aT^4\Delta v$ , whence  $p = \frac{1}{3}aT^4$  (a well known result). We can, in fact, write  $A = -pv$ . Let us denote by  $F$  the Zeta function of Gibbs, defined by the equation  $F = U - TS + pv$ , and now commonly called the free energy function. From this it follows that  $F = A + pv = 0$  for full radiation.

Denoting by  $H$  the heat function, defined by the equation  $H = U + pv$ , we obtain from the preceding results

$$H = aT^4v + \frac{1}{3}aT^4v = \frac{4}{3}aT^4v.$$

From this, we see that in the case of radiation  $H = TS$ . We can now draw up the following series of results for the five thermodynamic functions  $U$ ,  $H$ ,  $S$ ,  $A$ , and  $F$  ;

- (1)  $U = aT^4v$
- (2)  $H = \frac{4}{3}aT^4v$
- (3)  $S = \frac{4}{3}aT^3v$
- (4)  $A = -\frac{1}{3}aT^4v$
- (5)  $F = 0$

\* See, for example, Planck's *Wärmestrahlung*.

Expressed in terms of energy and temperature, we have

$$(6) \quad A = -\frac{1}{3}U$$

$$(7) \quad H = \frac{4}{3}U$$

$$(8) \quad S = \frac{4}{3}\frac{U}{T}$$

$$(9) \quad F = 0$$

We see that in the case of radiation,  $U = A + H$ .

We can readily show that the foregoing results are in agreement with the Gibbs-Helmholtz equation

$$-\Delta A + \Delta U = T \frac{\delta}{\delta T} \left( -\Delta A \right)_v.$$

Consider the change  $v \rightarrow v + \Delta v$  at temperature  $T$ . We have

$$-\Delta A + \Delta U = \frac{1}{3}aT^4 \Delta v + aT^4 \Delta v = \frac{4}{3}aT^4 \Delta v. \quad \text{Also } T \frac{\delta}{\delta T} \left( -\Delta A \right)_v =$$

$$T \frac{\delta}{\delta T} \left( \frac{1}{3}aT^4 \Delta v \right)_v = \frac{4}{3}aT^4 \Delta v.$$

In the integral form of the Gibbs-Helmholtz equation

$$\text{namely,} \quad \frac{\Delta A}{T} = \int \frac{-\Delta U}{T^2} dT + k,$$

we can show that  $k=0$ ; for  $\frac{\Delta A}{T} = -\frac{1}{3}aT^3 \Delta v$ ,

$$\text{and } \frac{-\Delta U}{T^2} = -aT^2 \Delta v, \text{ so that } \int \frac{-\Delta U}{T^2} dT = -\Delta v \int aT^2 dT =$$

$$-\frac{1}{3}aT^3 \Delta v.$$

$$\text{Thus in the case of full radiation } \Delta A = T \int_0^T \frac{-\Delta U}{T^2} dT, \quad \text{where}$$

$\Delta A$  and  $\Delta U$  refer to monothermic changes of volume at temperature  $T$ . Finally we may remark that it is easy to show by the consideration of a reversible Carnot cycle between  $T+\delta T$  and  $T$  that  $\frac{\delta W}{Q} = \frac{\delta T}{T}$  where  $\delta W$ =element of work yielded in the cycle and  $Q$ =heat taken in at the higher temperature.

Full radiation in thermal equilibrium constitutes, in fact, the simplest physical object (system) for thermodynamic treatment, and might well occupy a more prominent position in treatises on Physical Chemistry. It was a long time before chemists came to treat gases as really material systems possessing determinable mass and weight. Since radiation possesses a determinable mass, *i.e.*, that given by the well known Einstein equation, it offers us a "material" system whose thermodynamic properties and relations are very simple and are well worthy of ranking with those of the ideal gas in the mind of the student of chemistry. The density of radiation (in grams per c.c.) is given by the expression  $\frac{aT^4}{c^2}$ , where  $c$  = velocity of light in cms. per second  $= 3 \times 10^{10}$ . The value of  $a$  is  $7.3 \times 10^{-15}$ . Thus, for example, the temperature  $T$  at which radiation possesses a density equal to that of water at  $4^\circ$  is given by the equation

$$aT^4 = c^2, \text{ whence } T^4 = \frac{9 \times 10^{20}}{7.3 \times 10^{-15}} = \frac{9}{7.3} \times 10^{35}$$

$$\text{or } T = \sqrt[4]{\frac{9}{7.3}} \times 10^{8.75}. \text{ Thus } T \text{ is of the order of magni-}$$

tude of  $10^9$ , *i.e.*, a thousand million degrees. We can calculate similarly that radiation will require a temperature of the order of ten million degrees to reach a density one millionth of that of water at  $4^\circ$ . It is therefore only at excessively high temperatures, such as may be attained in stellar interiors, that radiation will evince its "materiality" by the possession of densities such as we are ordinarily familiar with. Nevertheless it is useful for the chemist to make such calculation, in order to convince himself that radiation is no immaterial and ghostly "effluvium," but a real physico-chemical system or object, subject to thermodynamical laws. In this connection calculations of pressure are much more striking than those of density. The pressure ( $p$ ) of radiation is given by the equation  $p = \frac{1}{3} aT^4$ , or  $p = 2.4 \times 10^{-15} T^4$  dynes per square centimetre. If we put  $T = 10^6$ ,  $p = 2.4 \times 10^9$  dynes/sq. cm. Putting one atmosphere pressure equal approximately to  $10^6$  dynes per sq. cm., we obtain  $p = 2400$  atmospheres. Thus at a temperature of one million degrees the pressure of radiation (against a perfectly reflecting surface) is greater than two thousand atmospheres. In a modern power station the steam pressure will not exceed 45 atmospheres, whilst the gas pressures used in technical chemical processes do not usually exceed

200 atmospheres. The high pressure exerted by radiation at relatively very low density is due to the factor  $c^2$  which occurs in the equation relating pressure and density.

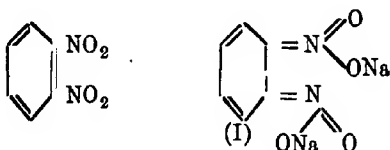
Thus if  $\rho$  be the radiation density and  $p$  the radiation pressure, we have as before  $\rho = \frac{aT^4}{c^2}$ ,  $p = \frac{1}{3}aT^4$ , so that  $\frac{p}{\rho} = \frac{1}{3}c^2$ , where  $c$  is the velocity of light. This equation may be compared with the corresponding equation for an ideal gas,  $\frac{p}{\rho} = \frac{1}{3}C^2$ , where  $C$  is a velocity such that  $C^2$  is the mean value of the square of the molecular velocity for all the molecules in the gas. Whereas in the case of a gas  $C^2$  is proportional to  $T$ , in the case of radiation  $c^2$  is a constant. In the language of the photon picture of radiation, the photons all move with the same constant velocity, namely the velocity of light, so that  $c^2$  is necessarily the mean value of the square of the photon velocity for all the photons of the radiation. From this point of view radiation may be regarded as a sort of ideal "photon gas," and its "equation of state" may be written in the form  $pv = \frac{1}{3}c^2$ , where  $v$  is the volume (in c.c.) containing one gram of radiation,  $p$  the Maxwellian radiation pressure (in dynes per sq. cm.) and  $c^2 = 9 \times 10^{20}$ . Previously we referred the thermodynamic functions to the quantity of radiation contained in an arbitrary volume  $v$  at a given temperature  $T$ . We found, for example, that in this case  $A = -pv$ . If we now refer the thermodynamic functions to *one gram* of radiation, we see that  $A = -\frac{1}{3}c^2$ ,  $U = c^2$ ,  $H = \frac{4}{3}c^2$ ,  $S = \frac{4}{3}\frac{c^2}{T}$ . Thus the quantities  $A$ ,  $U$ , and  $H$  per gram of radiation are constant, whilst the entropy per gram is inversely proportional to the temperature and approaches infinity as the temperature approaches the Kelvin zero.

Viewed from the point of view of inertial mass, radiation is therefore unlike an ordinary material system in its thermodynamic properties per unit of mass. Nevertheless it is "material" in the sense that it possesses energy and mass, and can push, press, and strike (momentum of a pulse of radiation).

## On a New Method for the Detection of some Polyhydroxyphenols.

BY PRAFULLA KUMAR BOSE.

It has been shown by the present author (Bose, *Z. anal. Chem.*, 1932, **87**, 110) that *o*-dinitrobenzene could be reduced to the deep violet quinonoid salt (I) by means of a reducing carbohydrate in alkaline solutions, a fact which may be made use of for the detection of the latter in minute quantities.



This observation apparently indicates a parallelism between Fehling's solution and *o*-dinitrobenzene so far as their reduction is concerned. To find out whether this similarity in behaviour is confined to the carbohydrate group alone or not, the action of *o*-dinitrobenzene towards various reducing agents has been studied. This part describes the action of *o*-dinitrobenzene towards some polyhydric phenols. The dihydroxybenzenes are known to reduce Fehling's solution irrespective of the orientation of OH-groups in the molecule. But their behaviour towards *o*-dinitrobenzene was not found to be identical. Thus, a mixture of resorcinol, *o*-dinitrobenzene and alkali solution did not develop any violet colour, the mixture turning brown when heated. Catechol and hydroquinone, on the other hand, gave the characteristic violet colour with the reagent in presence of sodium carbonate or a hydroxide solution in the cold. The colour, however, was rather dull in comparison with that produced by reducing sugars, specially when the concentrations of phenols were not very low. The minimum quantity detectable was found to be 0.000012 g. in 1 c.c. in the cases of hydroquinone and catechol, the concentrations of *o*-dinitrobenzene and sodium carbonate being 1 per cent. (in alcohol) and 25 per cent. respectively.

Phloroglucinol and orcinol behaved like resorcinol, while pyrogallol, gallic acid and tannic acid gave positive reactions. Even heavy molecules like catechin and quercetin developed a purplish-violet colour, under the usual conditions. It therefore follows that when there are at least two OH-groups in *ortho* or *para*-position to one another in the same benzene ring, a positive reaction is indicated, while substances having OH-groups in the *meta*-position to one another behave otherwise. It should be noted in this connection that substances having only one OH-group attached to a benzene ring do not respond to the test, unless an easily oxidisable group, such as  $\text{NH}_2$ , is also present in the molecule in suitable positions. It is believed that *o*-dinitrobenzene will prove of great value in locating phenolic OH-groups in organic compounds, both synthetic and natural.

The fact that *o*-dinitrobenzene may be reduced to the highly coloured quinonoid salt (I) by means of suitable reducing agents in alkaline solution may be utilised for its detection. Ordinary *m*-dinitrobenzene, produced by the nitration of nitrobenzene, contains appreciable amount of *o*-dinitrobenzene as an impurity. This is removed only with difficulty after repeated crystallisations. A specially purified specimen of *m*-dinitrobenzene did not develop any violet colour on treatment with a small quantity of sulphuretted hydrogen in warm aqueous-alcoholic ammonia solution. An ordinary sample from the market immediately turned deep violet under the above conditions. The intensity of colour depends roughly on the amount of *o*-dinitrobenzene present. When its concentration is very small, the violet colour does not persist for a long time.

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## On the Physical Unreality of the Terms used in Cataphoresis and the Fictitious $\zeta$ -Potential.

BY JAMES W. MCBAIN.

The characteristic or observable quantity in electrokinetics is the linear movement  $u$  relative to the bulk of the liquid or the framework of the system. In cataphoresis, now commonly called electrophoresis, this is the movement or mobility of the particle and may be determined directly or by means of a Hittorf migration experiment.\* In electro-osmosis  $u$  is the average velocity of flow of the liquid. Sometimes streaming potential,  $E_s$ , set up by a definite velocity of flow  $u$ , is measured instead.

In the Laing-McBain theory † of electrokinetics all the quantities hitherto observable have been simply and quantitatively related to  $u$ , the actual observable velocity for a given system. In this theory the equations are independent of the origin of the charges, whether due to adsorption, dissociation, or both.

In the classical theory, which is still commonly used, the electrokinetic phenomena are related to a supposititious quantity, the so-called  $\zeta$ -potential. Helmholtz did indeed regard his double layer as consisting of two parallel sheets of continuous electricity,  $\zeta$  being regarded as the actual difference in potential between them. His conception has long since been discarded, owing to the recognition that electrical charges in solutions are ionic and to the discrepancy between Helmholtz's conception and ionic dimensions and behavior. However, even in the more recent work of Gouy, Chapman, Smoluchowski, and Debye and Hückel, the Poisson equation is utilized to give results equivalent to that of a condenser carrying a continuous

\* The simplest method of measurement has been described by J. W. McBain and R. O. Williams, *Coll. Sym. Annual* (Baltimore, 1929), 1930, 7, 105; R. DuBois and A. H. Roberts, *J. Phys. Chem.*, 1931, 35, 3070).

† M. E. Laing, *J. Phys. Chem.*, 1924, 28, 673; J. W. McBain, *J. Phys. Chem.*, 1924, 28, 706; J. W. McBain and R. DuBois, *Z. Elektrochem.*, 1931, 37, 651; J. W. McBain and M. E. Laing McBain, communicated to *J. Amer. Chem. Soc.*, 1932; communicated to *Z. Phys. Chem.*, 1932; R. DuBois, communicated to *Z. Elektrochem.*, 1932.



uniform charge of electricity with the corresponding difference of potential equal to  $\zeta$  between the two plates of the condenser. The artificiality of this substitute for the actual state of affairs is enhanced by recognition of the fact, ably discussed by Mukherjee (*Phil. Mag.*, 1922, **44**, 321; *J. Indian Chem. Soc.*, 1925, **2**, 191), that the charges upon different parts of the same surface may be of opposite sign and are often rather far apart.

The comprehensive treatment and simple equations which refer all electrokinetic quantities to the actual value of  $u$ , which also relates them to surface conductivity and all the corresponding phenomena of electrochemistry, would appear to afford a definite and permanently necessary stage in the study of electrokinetics. No light is thrown upon the subject by further inserting the hypothetical values of  $\zeta$  which are derived only from empirical data.

The next stage is the analysis of the factors which account for the production of the observed values of  $u$ .

In the analogous case of ions a definite reference state is available in infinite dilution. It is unlikely that a similar reference state can be usefully set up for electrokinetic phenomena because the factors involved are so very much more numerous and varied. To mention but one, the charge of an ion at infinite dilution is fixed and is unaffected by changes in environment or  $p_H$  or by additions of other electrolytes or of capillary-active substances all of which greatly affect the charge on an interface not only in magnitude but even in sign. There is no such thing as infinite dilution for a polyvalent particle which can dissociate or adsorb at numerous points of its surface. For these reasons it will in general always be necessary to proceed from observed values of  $u$  and by suitable supplementary measurements such as surface conductivity,  $p_H$ , ultrafiltration, etc., determine the magnitude of the many factors such as the source and nature of the free and bound charges. Attempts to take  $\zeta$ -potential and the hypothetical condensers and all the derived formulae literally lead to magnitudes which are obviously incompatible with the dimensions of real ions, molecules and charges. This has been shown, for example, by McBain and DuBois\* with absolute measurements of

\* J. W. McBain and R. DuBois, *Z. Elektrochem.*, 1931, **37**, 661; R. DuBois, communicated to *Z. Elektrochem.*, 1932; J. W. McBain and C. R. Peaker, *Proc. Roy. Soc. (London)*, 1929, **A**, **123**, 394; *J. Phys. Chem.*, 1930, **34**, 1033; J. W. McBain, C. R. Peaker and A. M. King, *J. Amer. Chem. Soc.*, 1929, **51**, 3394.

surface conductivity. We shall now show that inspection of the commonly used formula for cataphoresis leads to the same conclusion.

It is well known, and it has been pointed out by many writers, that Stokes' law is wholly inadequate by itself as a means of evaluating the charge on a colloidal particle. The results are always of a lower order of magnitude than the charges known to be present, being often a thousand or ten thousand times too small. Now workers in electrokinetics and colloids commonly employ the Debye-Hückel formula for the cataphoresis or electrophoresis of spherical particles.†

$$u = \frac{XD\zeta}{6\pi\eta}$$

It has not, however, been recognised that this is merely Stokes' law with a wholly inadequate correction. It is Stokes' law with a correction which can only modify it by 50 or 60 per cent., but omitting the correction which would alter it by the remaining 49.9 or 39.99 per cent., thus altering the order of magnitude. Paine ‡ has pointed out the omission but did not mention its significance. Indeed, where the corrections are of such magnitude their theoretical basis is inadequate and the formula is invalidated.

For an ion, Debye and Hückel introduced not only the correction to Stokes' law for viscous drag (their unfortunately named electrophoretic effect) but also for the relaxation of the ionic atmosphere, writing the equation \* for an ion or particle of radius  $r$

$$X\epsilon = 6\pi\eta ru + \frac{X\epsilon r\kappa}{1+r\kappa} + \frac{e^2\kappa\rho u}{6DkT(1+r\kappa)}$$

where  $X$  is the electrical field or potential gradient,  $\epsilon$  the total charge attached to the particle,  $\eta$  the viscosity,  $u$  the actual velocity of the central ion or particle as discussed above,  $\kappa$  equals the reciprocal of

† M. V. Smoluchowski, "Handbuch der Elektrizität und des Magnetismus," by L. Graetz, 1914, Bd. II, Lieferung 2, p. 384; P. Debye and E. Hückel, *Physikal. Z.*, 1924, 25, 60, 204.

‡ H. H. Paine, *Proc. Cambridge Phil. Soc.*, 1932, 28, Part 1, 90. E. W. Russell (*J. Agric. Sci.*, 1932, 23, Part 1, 182) has made a similar observation and adds numerous criticisms of the classical treatment.

\* P. Debye and E. Hückel, *Physikal. Z.*, 1923, 24, 316, equation 42; E. Hückel, *Physikal. Z.*, 1924, 25, 210.

the equivalent thickness of the ionic atmosphere,  $D$  is the dielectric constant (commonly assumed to be equal to that of water although possibly more than a decimal point smaller),  $k$  the Boltzmann constant,  $T$  the absolute temperature, and  $\rho$  the average friction constant for the ions of the ionic atmosphere surrounding the central ion or particle,  $\rho$  being equal to the mechanical force required to make an ion travel with unit velocity. It will be noted that since the last two terms each contain the fraction  $\frac{1}{1+\tau\kappa}$ , both the electrophoretic and relaxation terms are affected in the same way by a finite value of  $r$  and are multiplied by this factor.

The Debye-Hückel picture is equivalent electrically to a fictitious spherical condenser of inner radius  $r$  and outer radius  $r + \frac{1}{\kappa}$ , the distance between plates being  $\frac{1}{\kappa}$ . Hence  $\zeta$  is regarded as the difference in potential between the surface and the ionic atmosphere, and, taking

$$D\zeta = e \left( \frac{1}{r} - \frac{1}{r + \frac{1}{\kappa}} \right) = \frac{e}{r(1 + \tau\kappa)}$$

where  $e$  is the hypothetical charge corresponding to the hypothetical  $\zeta$  and to the equivalent thickness of ionic atmosphere  $\frac{1}{\kappa}$  which depends greatly upon the concentration, their equation

$$u = \frac{XD\zeta}{6\pi\eta}$$

is identical with

$$u = \frac{Xe}{6\pi\eta r} \left( 1 - \frac{\tau\kappa}{1 + \tau\kappa} \right)$$

Reinserting the relaxation term, Paine sets

$$u = \frac{Xe \left( 1 - \frac{\tau\kappa}{1 + \tau\kappa} \right)}{6\pi\eta b + \frac{e^2 \kappa \rho}{6DkT(1 + \tau\kappa)}}$$

This assumes as an approximation the form

$$\frac{XD\zeta}{6\pi\eta} \left[ 1 - \frac{\rho r\kappa(1+r\kappa)D\zeta^2}{36\pi\eta kT} \right]$$

Taking  $a$  as the radius of an ion in the atmosphere and Stokes' law as applicable to it,  $\rho = 6\pi\eta a$  for unit velocity, Paine puts this equation in the form

$$u = \frac{Xe}{6\pi\eta r} \left[ 1 - \frac{r\kappa}{1+r\kappa} - \frac{a}{r} \cdot \frac{e^2\kappa}{6DkT(1+r\kappa)} \right]$$

in order to show that, as with ions, the second correction is almost as important as the first. It is tacitly assumed that  $\eta$  is the same in all three terms. We have here gone further in pointing out that the application of both correction terms together must change Stokes' law by an order of magnitude; and that if one is left out, it is almost as bad as to go back to the simple Stokes' law altogether.

Most of the  $\zeta$ -potentials recorded in the literature are calculated for observed values of  $u$  by substituting in the formula  $\frac{XD\zeta}{4\pi\eta}$  and some of the more recent ones by substituting the observed value in  $\frac{XD\zeta}{6\pi\eta}$ , the shape of the particles being unknown, whereas it is now proven that a still further formula is demanded. There is likewise grave uncertainty as to the values of  $D$  and  $\eta$  in the immediate neighbourhood of the charges. Surely it is better to hold the unambiguous directly measured value of  $u$  which gives immediately a quantitative expression of all electrokinetic phenomena rather than to introduce a fictitious  $\zeta$  with all this arbitrary uncertainty, especially since the magnitude and even sign of the real potential differences may change from point to point on a colloidal particle or other surface. In discussing ordinary ions, real quantities are adhered to and no one introduces the  $\zeta$ -potential, although the conditions are exactly similar in kind and very much nearer the truth in degree.

#### *Summary.*

It is pointed out that all the real observed quantities in electrokinetics are summed up in the directly observed linear velocity  $u$  and that not only has the so-called  $\zeta$ -potential never been measured but

that its calculation is arbitrary and attended with grave uncertainty. In many, or possibly all, cases it is wholly fictitious.

The Debye-Hückel formula for cataphoresis, now usually employed for obtaining the  $\zeta$ -potential by calculation from the observed velocity  $u$ , is Stokes' law with an inadequate correction, leaving out another that is equally important. The corrections must be so large as to change the result by an order of magnitude and to invalidate that formula.

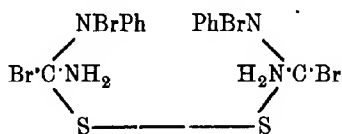
DEPARTMENT OF CHEMISTRY,  
STANFORD UNIVERSITY,  
CALIFORNIA.

## The Interaction of Aromatic Thiocarbamides with Bromine.

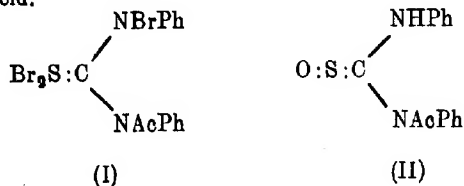
By ROBERT FERGUS HUNTER.

The interaction of halogens with thiocarbamides has attracted the attention of several investigators at different times (Otto, Hofmann, Belstein and Kurbatow, Claus, Storch MacGowan), but the credit of first examining such reactions in inert media belongs essentially to Hugershoff (*Ber.*, 1901, **34**, 3130).

Hugershoff observed that when a chloroform solution of phenylthiocarbamide is treated with bromine, hydrogen bromide is evolved with the production of an orange coloured bromo-addition compound which he first regarded as the bromocarbaminophenylbromoamino-disulphide



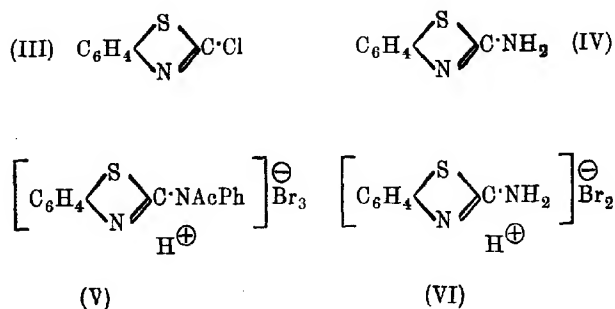
which gave a colourless base on reduction with sulphurous acid, which he presumed to be the carbaminophenyliminodisulphide,  $\text{NH}_2 \cdot \text{C}(\text{:NPh}) \text{S} \cdot \text{S}(\text{:NPh}) \text{C} \cdot \text{NH}_2$ . In a similar manner, Hugershoff and König (*Ber.*, 1901, **34**, 3136) obtained a tribromide from acetyldiphenylthiocarbamide to which they assigned the formula(I) which yielded an alleged sulfoxide (II) on treatment with sulphurous acid.



At a later date, however, Hugershoff discovered that the supposed carbaminophenyliminodisulphide had none of the properties associated with the parent substance of this group (*Ber.*, 1903, **36**, 3121), but was actually identical with 1-aminobenzthiazole (IV)

obtained from 1-chlorobenzthiazole (III) and ammonia (Hofmann, *Ber.*, 1879, 12, 1123; 1880, 13, 8). Furthermore, the supposed sulphoxide (II) was found to be identical with 1-acetanilino benzthiazole obtained from the acetylation of the anilino base prepared by Hofmann's method (*loc. cit.*).

The curious tribromide obtained by Hugershoff and König from the acetylthiocarbamide has recently been proved by Dyson, Hunter and Soyka (*J. Chem. Soc.*, 1929, 459) to be the *hydrotribromide* of 1-acetanilino benzthiazole (V).



The supposed bromocarbaminophenylbromoaminodisulphide of Hugershoff has been shown to be a *hydrodibromide* of 1-aminobenzthiazole, which can readily be prepared from the hydrobromide of the amino base and bromine (Hunter, *J. Chem. Soc.*, 1930, 125).

The constitution of this substance is a matter of considerable importance. In the first place, it must be emphasised that the hydrobromide is a definite *compound*, and is *not* a eutectic mixture of 1-aminobenzthiazole hydrobromide and a hypothetical hydrotribromide. This is shown by the fact that it separates from different concentrations of the components (above a certain minimum concentration of the halogen), and from solutions of the components in different solvents (*loc. cit.*). Moreover, all attempts to isolate the hypothetical hydrotribromide of 1-aminobenzthiazole by using a large excess of bromine have proved unsuccessful, and the extraordinary stability of the hydrodibromide is quite incapable of interpretation on any "physical mixture" explanation. It has therefore been suggested that the hydrodibromide possesses the formula (VI),

containing the hitherto unknown  $\text{Br}_2\text{-ion}^\ominus$ , and involving the operation of a "lone singlet" linkage.

The investigation of similar hydrodibromides of the 5-bromo-1-alkylaminobenzthiazole series is now in progress and will shortly be published from these laboratories.

During his final investigation of the bromination of arylthiocarbamides in chloroform, Hugershoff observed that thiocarbanilide yielded a red unstable tetrabromide of 1-anilinobenzthiazole, whilst the *s*-di-*o*- and *s*-di-*p*-tolylthiocarbamides gave rise to similar compounds which yielded the corresponding 1-toluidinomethylbenzthiazoles on reduction with sulphurous acid (*Ber.*, 1903, 36, 3121).

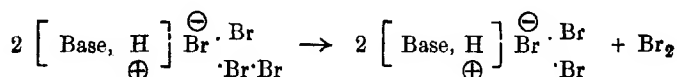
These experiments were carefully reinvestigated by the author in 1924, who discovered that the unstable red bromo-addition compound obtained from *s*-di-*o*-tolylthiocarbamide had the composition of a hexabromide of 1-*o*-toluidino-3-methylbenzthiazole, whilst that obtained from *s*-di-*p*-tolylthiocarbamide appeared to be a tetrabromide of 1-*p*-toluidino-5-methylbenzthiazole. It was also observed that these unstable bromo-addition compounds, including the tetrabromide obtained from thiocarbanilide by Hugershoff, readily lost bromine yielding *unstable yellow tribromides* (Hunter, *J. Chem. Soc.*, 1925, 127, 2033).

It is unfortunate that the possibility of these compounds being hydroperbromides was never entertained, mainly on account of the fact that such a possibility necessitated the formulation of compounds with an odd number of valencies, and as a consequence of this a number of erroneous formulae were suggested for these compounds and their numerous homologues and derivatives which were prepared in later investigations (Hunter, *J. Chem. Soc.*, 1925, 127, 2270; 1926, 1385, 1401, 2951; Hunter and Soyka, *ibid.*, p. 2958; Dyson, Hunter and Morris, *J. Chem. Soc.*, 1927, 1186; Hunter and Styles, *ibid.*, p. 1209; Hunter and Styles, *J. Chem. Soc.*, 1928, 3019; Hunter and Pride, *J. Chem. Soc.*, 1929, 943). It has now been definitely established that the bromo-addition compounds of thiazole derivatives obtained by brominating arylthiocarbamides in chloroform are invariably *hydroperbromides* (Dyson, Hunter, and Soyka, *J. Chem. Soc.*, 1929, 459; Hunter, *J. Chem. Soc.*, 1930, 125) and it is therefore suggested that the hydrotetrabromides of 1-anilinobenzthiazole and 1-*p*-toluidino-5-methylbenzthiazole have formulae of

the type,  $\left[ \text{Base}, \text{H} \right]^\oplus \text{Br}_4^\ominus$ .



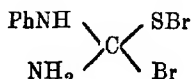
On the basis of this, the ready elimination of bromine from these compounds with the production of stable hydrotribromides can be interpreted on the generally accepted view that singlet linkages derive stability from mutual association (compare Sugden, *J. Chem. Soc.*, 1927, 1173).



The main difficulty which presents itself in relation to this hypothesis is, of course, the formulation of odd-electron molecules.

With regard to the hydrohexabromide of 1-*o*-toluidino-3-methylbenzthiazole and similar compounds; these substances are so unstable that it is apparently impossible to obtain absolute evidence that they are not solid solutions of bromine and a hydroperbromide of a lower order. In any case, it is undesirable to attempt to base far-reaching conclusions on the results of experiments of the type which have so far been recorded.

Regarding the mechanism of the synthesis of 1-aminobenzthiazole from phenylthiocarbamide and bromine, Hugershoff suggested (*loc. cit.*), that the first action of bromine on phenylthiocarbamide in chloroform is the formation of a labile dibromo-addition product,



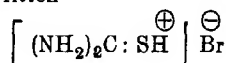
which eliminates two molecules of hydrogen bromide giving the thiazole derivative.

The reaction between phenylthiocarbamide and bromine is unfortunately, much too rapid to permit an investigation of its mechanism. For this reason, Dyson, Hunter, and Soyka examined the case of *s*-di-*p*-bromophenylthiocarbamide which normally yields the hypopentabromide of 5:4'-dibromo-1-anilinobenzthiazole on being heated with excess of bromine in chloroform for some 20 to 30 minutes (*loc. cit.*). It was found that the first action of bromine on *s*-di-*p*-bromophenylthiocarbamide was to yield a *perbromide* of the thiocarbamide, which could not be converted into 5:4'-dibromo-1-anilinobenzthiazole by treatment with strong alkalis, which would be expected to remove hydrogen bromide from an intermediate bromo-addition compound of the type suggested by Hugershoff,

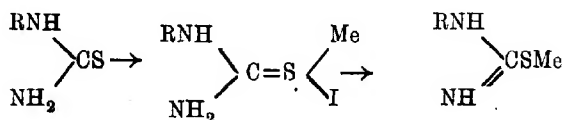
although it regenerated the original thiocarbamide on reduction with sulphurous acid. It is therefore inferred that the perbromide of *s*-di-*p*-bromophenylthiocarbamide cannot have a structure containing the  $\cdot\text{CBr} \cdot\text{SBr}$  complex.

In considering the mechanism of the reaction discovered by Hegershoff, it is necessary to refer to certain recent investigations on the structure of the thiocarbamides.

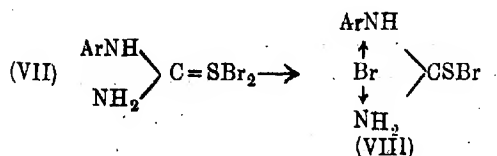
In the first place, the oxidation of tetrasubstituted thiocarbamides to disulphide derivatives (Lecher, *Annalen*, 1925, **445**, 86), invalidates the arguments in favour of the classical formula,  $\text{NH}_2\cdot\text{C}(\text{SH})\cdot\text{NH}$ , for thiocarbamide, which rest essentially on the oxidation of thiocarbamides containing a hydrogen atom to disulphides. The X-ray analysis of thiocarbamide itself (Hendrick, *J. Amer. Chem. Soc.*, 1928, **50**, 2455) moreover indicates, that the crystalline form of the compound has the thioamide structure,  $\text{CS}(\text{NH}_2)_2$ . The salts of the thiocarbamides (Dixon, *J. Chem. Soc.*, 1917, **111**, 318), such as the hydrobromide of thiocarbamide, can therefore be written

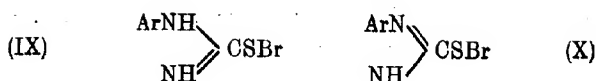


and are evidently the reactive units in the classical oxidation experiments on the compounds. It may be noted that the suggestion that thiocarbamides are probably alkylated through the thioamide form to give S-alkyl derivatives, was made by Dixon and Taylor as long ago as 1912 (*J. Chem. Soc.*, **101**, 2502).

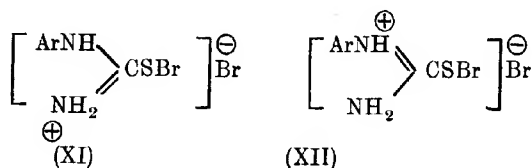


It is therefore probable that the first action of bromine on an arylthiocarbamide in an inert solvent is to produce a dibromide (VII), in which bromine subsequently migrates as ion to the nitrogen atoms, yielding the salt (VIII), which can give rise to either of the tautomerides (IX) or (X) by incipient loosening of hydrogen bromide.



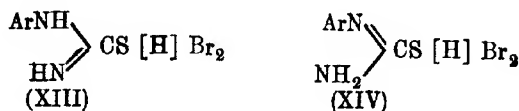


The eliminated hydrogen bromide will then combine with the doubly bound nitrogen atoms in the isomers (IX) and (X) (Pyman, *J. Chem. Soc.*, 1923, **123**, 3359), yielding the salts (XI) and (XII).



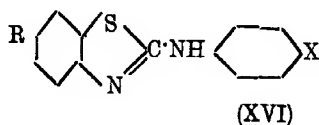
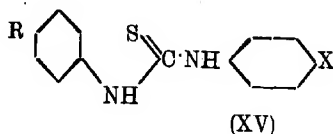
Burtles and Pyman have, however, shown that both 2:4- and 2:5-diphenylglyoxalines give rise to identical salts, indicating that the anions of amidine tautomers are electromeric (*J. Chem. Soc.*, 1923, **123**, 362), and it is therefore evident that the salts (XI) and (XII) will be identical; the positive charge produced by conversion of the amidine into the ammonium condition being presumably located to the extent of about a half positive charge on each nitrogen atom. Elimination of the bromine of the bromothiol grouping of the salt (XI) or (XII) along with the *ortho*-hydrogen atom of the aromatic nucleus then yields the hydrobromide (or hydroperbromide) of the aminobenz-thiazole.

Another way of arriving at the same result is to assume that once bromine has been added to the thioamide form of the thiocarbamide the resulting bromo-addition compound (VII) tautomerises yielding (XIII) and (XIV), which then eliminate hydrogen bromide in the usual way, giving the salt (XI or XII), through which cyclisation takes place.



Considerable interest attaches itself to the effect of substituents on the direction of cyclisation in thiocarbamilides containing mixed substituents (XV). Assuming that thiazole formation takes place by the mechanism which has just been outlined, it is clear that the effect of

substituents will depend on their capacity for assisting or inhibiting the removal of hydrogen as hydrogen bromide from the carbon atom which is *ortho* to the nitrogen atom which becomes nuclear during ring formation.



It has been found (Dyson, Hunter, and Soyka, *J. Chem. Soc.*, 1929, 458; Hunter and Jones, *J. Chem. Soc.*, 1930, 2190) that the bromination of *p*-nitro-, *p*-chloro-, *p*-bromo-, and *p*-ethoxy-*s*-diphenylthiocarbamides (XV, R=H; X=NO<sub>2</sub>, Cl, Br, and EtO) and of *p*-nitro-, *p*-bromo-, and *p*-ethoxy-*s*-*p*-tolylthiocarbamides (XV, R=Me; X=NO<sub>2</sub>, Br, and EtO) yields benzthiazole derivatives produced by ring closure either on the unsubstituted benzene nucleus or on the nucleus containing the methyl group (XVI, R=H; X=NO<sub>2</sub>, Cl, Br, EtO and R=Me; X=NO<sub>2</sub>, Br, and EtO respectively). Since the *s*-*p*-chloro-*p'*-bromo-, *s*-*p*-nitro-*p'*-bromo-, and the *s*-*p*-bromo-*p'*-ethoxy-diphenylthiocarbamides (XV, R=Br, X=Cl; R=Br, X=NO<sub>2</sub>; R=EtO, X=Br) give rise to 5-bromo-4'-chloro-, 5-bromo-4'-nitro-, and 4'-bromo-5-ethoxy-1-anilinobenzthiazoles respectively, the inhibitory effect of substituents on benzthiazole formation from thiocarbamides is therefore in the order: NO<sub>2</sub> > Cl > Br > EtO > Me.

The reason why the *meta*-derivative nitro group does not produce ring closure on the nucleus opposite to that favoured *o*-*p*-directing substituents is evidently due to the fact that the nitro group does not really favour *meta* substitution at all, but rather that it favours *o* *p*-substitution less. This is of course, embodied in the general conception (Ingold, *Annual Reports of the Chemical Society*, 1926, 134) that *meta* substitution is a residual effect produced by the disappearance of free affinity from the *o*-*p*-positions.



## Nitrification in Soil and in Atmosphere. A Photochemical Process.

BY N. R. DHAR AND G. GOPALA RAO.

It is well known that ammonia, ammonium salts and other complex nitrogenous compounds are slowly oxidised in the soil to nitrite and nitrate. This oxidation of ammonia and its compounds is known as nitrification and is one of the most important processes from the view point of soil fertility.

It is now universally believed that nitrification in soil is entirely due to the action of living organisms, the nitrifying bacteria. The researches of Warington (*J. Chem. Soc.*, 1878, **33**, 44; 1879, **35**, 429; 1891, **59**, 484), P. F. and G. C. Frankland (*Proc. Roy. Soc.*, 1890, **47**, 296) and Winogradsky (*Ann. Inst. Pasteur*, 1890, **4**, 213, 257; 1891, **5**, 92, 577; *Compt. rend.*, 1890, **110**, 1013), who was the first to obtain nitrifying bacteria of the soil in pure culture, led to the view that nitrification was really due to the joint action of two organisms—one converts ammonia and its compounds to nitrites and the other converts nitrites to nitrates but has no effect on ammonium salts.

Recently Gopala Rao and Dhar (*Soil Science*, 1931, **31**, 379; *Z. anorg. Chem.*, 1931, **199**, 422) have advanced the view that nitrification in soil must be partly photochemical in nature taking place at the surface of the soil in presence of sunlight. This view has been based on our experiments on the photo-oxidation of ammonia and its salts in sunlight and in mercury vapour lamp light in presence and in absence of photosensitisers.

In this communication we have summarised our published work and have adduced more direct and indirect experimental evidence in support of our views.

### *Oxidation of Ammonia and its Salts.*

We have observed that ammonia is slowly oxidized in aqueous solution to nitrite, when exposed to the light from a quartz mercury vapour lamp and copper arc and more slowly in sunlight. The

oxidation of ammonia solutions takes place even in light filtered through a 5% quinine sulphate solution of 4 cms. thickness, which cuts off radiations shorter than 4200Å. Ammonium salts are also oxidised to nitrites, the reaction being slower in the case of the sulphate and chloride than with phosphate and carbonate.

*Oxidation of Ammonia and its Salts in Sunlight in the Presence of Photosensitisers.*

The velocity of the photo-oxidation of aqueous solutions of ammonia and its salts is considerably increased by the presence of photosensitisers like titania, zinc and cadmium oxides, alumina, silica, magnesia, etc. Titania is the most and silica is the least active in this photo-oxidation. The  $p_H$  of the solution has a profound influence on the reaction velocity; alkalinity increases the velocity of the oxidation of ammonium salts and acidity decreases the oxidation. The velocity of the oxidation is greater in quartz vessels than in glass ones. The accumulation of nitrite appears to have no influence on the velocity of the oxidation of ammonia and its salts.

*Oxidation of Urea and other Nitrogenous Compounds.*

We have observed that aqueous solutions of urea, acetamide, hydroxylamine hydrochloride, hydrazine hydrochloride, ethylamine, methylamine, etc., are also oxidised to nitrite in presence of sunlight and zinc oxide. The oxidation of these compounds is slower than that of ammonium salts.

The conversion of urea and the other nitrogenous compounds into ammonia under the action of light appears to be the first stage in their oxidation to nitrite. Aqueous solutions of alanine, glycine and aspartic acid are converted into ammonia in presence of light. These results indicate that ammonification in soil is also partly photo-chemical in nature.

*Oxidation of Ammonium Salts in Sunlight at the Surface of Sterilized and Unsterilized Soil.*

Very recently Dhar, Bhattacharya and Biswas have carried on experiments on the oxidation of different ammonium salts by exposing them to light after mixing them with soil. Known weights of soil were mixed with definite amounts of ammonium salts and water and exposed to sunlight in glass jars for a definite period. In order to determine whether any oxidation takes place in the

absence of light, some glass jars and their covers were completely covered with a thick coating of Japan black enamel so as to cut off light completely and soil and ammonium salts under identical proportions were also placed in the blackened jars. Experiments were also carried on with the same soils after sterilizing them with chloroform or by heating them to  $200^{\circ}$  for several hours. Our experimental results show that large amounts of the ammonium salts were converted into nitrite in presence of light and air but very little nitrite was obtained in the blackened bottles containing the unsterilized or sterilized soils. The ammonium compounds mixed with the sterilized soils were also converted into nitrites in presence of light practically to the same extent as in the unsterilized soils.

*Comparative Rates of Bacterial and Photochemical Nitrification.*

The amounts of nitrite formed in the photosensitised oxidation of ammonia and its salts in presence of zinc oxide and sunlight appear to be much more than the amounts of nitrite formed in the bacterial nitrification experiments of Warington (*J. Chem. Soc.*, 1891, **59**, 49) and the more recent experiments of Cutler and Mukerji (*Proc. Roy. Soc.*, 1931, **B**, **58**, 384). In one of their best experiments, these workers obtained 0.25 mg. of nitrite nitrogen per litre in 144 hours from a solution of ammonium sulphate containing 0.02 g. nitrogen in 100 c.c.; whereas in 3 hours we have obtained 3.22 mg. of nitrite nitrogen with a solution of ammonium sulphate containing 0.28 g. nitrogen in 100 c.c.

*Discussion.*

Hitherto, it has been generally believed that nitrification in the soil is entirely due to bacteria. From the foregoing results it is clear that nitrification is, at least, partially photochemical in nature taking place at the surface of various soil ingredients, which absorb the solar radiations. (*vide a, b and c.*)

The following facts, which are inexplicable from the bacterial view point of nitrification, are readily explained from our photochemical theory (*vide a', b' and c'*).

(a) Several authors have observed that a concentration of nitrite or ammonia greater than 0.3 p.c. interferes with the bacterial nitrification process. But in certain localities, the so-called nitre spots, a high concentration of nitrite and nitrate (as much as 5 p.c. of the bulk of the soil) has been observed.



(b) The nature of the soil has been found to exert a marked influence on nitrification.

(c) A periodic variation of the nitrite and nitrate content of soils has been observed by several workers both in the Northern and Southern Hemispheres. The amount of nitrite and nitrate of soils rises to a maximum in summer and falls to a minimum in the winter.

(a') It has been already stated that in the photochemical oxidation of ammonia and its salts, the amount of nitrite formed does not influence the velocity of the oxidation and thus the photochemical theory sets no limit to the amount of nitrite formed and the accumulation of nitrites and nitrates in large amounts in the nitre spots is explained.

(b') Titania has been found to be the best photocatalyst in the photo-oxidation of ammonia and its salts. Hence soils containing titania are likely to be more fertile than those containing only silica, alumina etc., which are not efficient photocatalysts. In agreement with this view, Geilman (*J. Landw.*, 1920, 68, 107) has reported that most fertile soils contain titania in quantities as large as 0.3–0.6 p.c. It also occurs in the ashes of all plants up to 0.27 p.c.

Several workers have reported that nitrification is most active at the surface of the soil. According to Prescott and Piper (*J. Agric. Sci.*, 1930, 20, 516) nearly 80 p.c. of the nitrate accumulation takes place in the first  $3\frac{1}{2}$  inches depth of the soil. As light is essential for nitrification, it is natural that the oxidation will be greatest at the surface where maximum light absorption takes place.

(c') *Periodicity of Nitric Nitrogen in Soil.*—It has already been stated that the nitrite and nitrate content of soils rises to a maximum in summer and falls to a minimum in the winter (compare Batham and Nigam: *Soil Science*, 1930, 29, 181). If nitrification is entirely due to bacteria, a periodic variation as observed by different workers would not be expected, because according to the experiments of Warington (*Chem. News.*, 1877, 36, 268), light hinders the activity of nitrifying organisms and as there is more sunlight in summer, there ought to be less nitrification. Moreover, in the summer months, the temperature of the soil easily reaches 50°, specially in the tropics and this high temperature should be detrimental to the nitrifying organisms, as the optimum temperature for their action is about 25°.

In the following tables, the results obtained by different workers on the periodic variation of nitrites and nitrates are summarised:

TABLE I.

*Relative nitrate accumulation in the soil during different months, the lowest analytical number being taken as 100.*

NORTHERN HEMISPHERE.														
Country.	Year.	Name of worker	Jan.	Feb.	Mar.	Apr.	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.
Texas (U. S.)	1913-16	Fraps	100	171	121	121	471	621	593	443	321	486	121	121
Germany	1920	Lemmermann and Wichers	103	104	110	206	210	—	274	138	—	134	122	100
Germany, Oberholz	1912-13	Green	—	111	123	132	134	—	125	114	121	107	103	102
England	1912	Russel	—	125	113	142	118	205	237	—	100	—	—	—
India, Cawnpore	1923-24	Batham and Nigam	100	112	106	124	148	174	191	103	100	—	114	—
SOUTHERN HEMISPHERE.														
South Africa	1919-20	Hall	459	186	100	130	123	308	337	222	—	386	351	671
New South Wales	1921-22	Taylor	470	385	425	—	—	150	260	100	155	180	270	170

TABLE II.  
Nitrate accumulation during different months grouped according to seasons.

NORTHERN HEMISPHERE																		
Country.	Year.	Name of worker.	Winter			Average.	Spring			Average.	Summer			Average.	Autumn			
			Dec.	Jan.	Feb.		Mar.	Apr.	May		June	July	Aug.		Sep.	Oct.	Nov.	
Germany, Oberholz,	1912-13	Green	102	...	111	106	123	132	134	130	...	125	114	119	121	107	103	110
Texas	1913-16	Fraps	121	100	171	131	121	121	471	238	621	593	443	552	321	486	121	309
Germany	1920	Lemmermann and Wichers	100	108	104	104	110	206	210	175	142	274	138	186	...	131	122	123
India, Cawnpore	1923-24	Batham and Nigam	...	100	112	106	106	124	148	126	174	191	103	156	100	...	114	107
Mean of averages	...	...	...	...	...	113	...	...	...	164	...	...	...	229	...	...	...	163
SOUTHERN HEMISPHERE																		
Country.	Year.	Name of worker.	Summer			Average.	Autumn			Average.	Winter			Average.	Spring			
			Dec.	Jan.	Feb.		Mar.	Apr.	May		June	July	Aug.		Sep.	Oct.	Nov.	
South Africa	1919-20	Hall	671	459	186	439	100	130	123	116	308	337	232	289	...	386	351	368
New South Wales.	1921-22	Taylor	170	470	385	342	425	...	...	...	150	260	100	170	155	180	270	202
Mean of averages	...	...	...	...	...	390	...	...	...	271	...	...	...	229	...	...	...	285

The solar activity in the Northern Hemisphere is greatest on June 22, after which it decreases steadily till December 22, when it again gradually rises. Thus the solar activity is greatest in the months of June and July and least in the months of December and January in the Northern Hemisphere. An examination of the first portions of Tables I and II shows that in most cases the nitric nitrogen content of the soil is at its maximum in June or July and its minimum is in December or January. This is also clear from the curves (Figures 1 and 2).

FIG. 1.

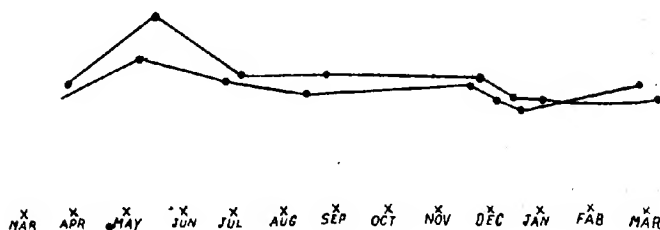
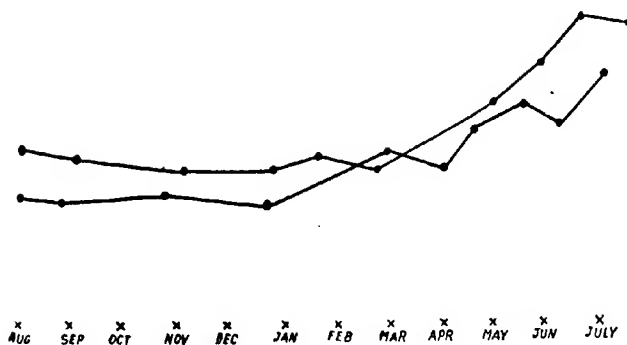


FIG. 2.

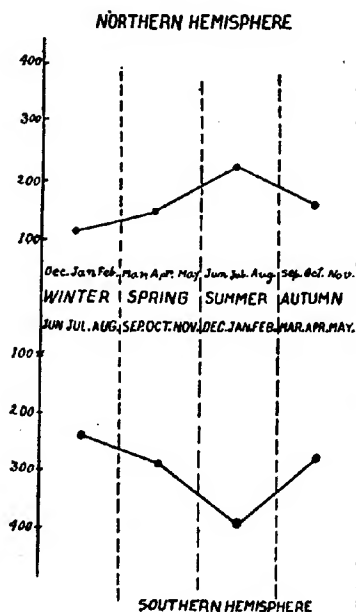


Moreover, the average of the amounts of nitrate in autumn and spring in Northern Hemisphere is more or less the same and is greater than that in winter and less than that in the summer, because the earth receives nearly the same measure of solar activity in spring and autumn and this is greater than that received in winter and less than that in the summer.

*Reciprocal Variation of Nitrate in Soils of the Northern and Southern Hemispheres.*

In the Southern Hemisphere, the solar activity is greatest in December and January and least in June and July. From the figures in Table II, it will be evident that the greatest amount of nitrate occurs in December and January and least in June and July in the Southern Hemisphere. The two Hemispheres are reciprocal in their seasons and they are also reciprocal in the nitrate content of their soils during different seasons of the year. This point is well illustrated in Fig. 3. Recently Prescott and Piper (*J. Agric. Sci.*, 1930, 20, 516) working in South Australia have shown that nitrate accumulation was largest in the months of November and December and least in the months of June and July. It must be remembered that in Australia, the maximum solar activity occurs in November and December, this being the hottest part of the year. Our general contention that nitrification is maximum in the summer and minimum in the winter is confirmed by the recent experiments of Prescott and Piper. Moreover, our views appear to be supported by the experiments of Mortenson and Duly (*Soil Science*, 1931, 32, 195) who have shown that the amount of nitrate in soil increases on illumination by ultraviolet light.

FIG. 3.



From the foregoing pages, it is evident that nitrification in soil can take place in the complete absence of bacteria and may be due to the photo-oxidation of ammonia and its salts by air at the surface of the soil in presence of sunlight.

#### *Nitrification in Air.*

In a recent communication (*Z. anorg. Chem.*; 1931, 199, 422) we have advanced the view that the ammonia existing in atmosphere is photochemically oxidised to nitrite and nitrate by air in presence of the ultraviolet rays of the sun. This photochemical oxidation of ammonia is the main source of nitric nitrogen in the atmosphere.

FIG. 4.

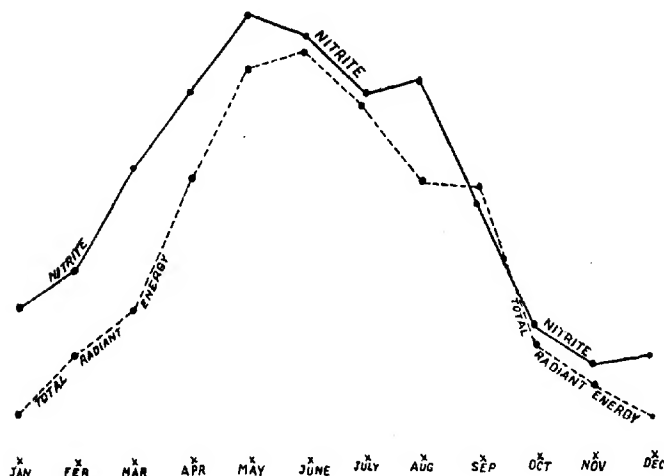


Figure 4 contains two curves, one showing the variation of the total radiant energy from month to month, the other curve shows the change of the nitric nitrogen content of the atmosphere during the year (compiled from the observations made at the Radcliffe Observatory, Oxford). The two curves follow each other very closely. It appears that the variation in the nitric nitrogen of the atmosphere with variation of the intensity of sunlight is more close than that of the soil, for in the atmosphere there is no interfering agency as the bacteria. In the soil, nitrification is due to two agencies, viz., the bacteria and sunlight, whereas in the atmosphere, nitrification is due to the action of sunlight only.

The photochemical theory of the formation of nitric nitrogen in the atmosphere satisfactorily explains the following observations:

(1) The proportion of nitric nitrogen in the atmosphere is greater at high than at low altitudes.

(2) There is a seasonal variation of the nitric nitrogen in air, the maximum occurs in the summer and the minimum in winter.

(3) The proportion of nitric nitrogen in rain water is much greater in tropical countries than in temperate regions.

(4) The ratio of nitric to ammoniacal nitrogen in the atmosphere is much greater in tropical countries than in colder countries.

Ammonia occurs to an appreciable extent in the atmosphere. Fowler and Gregory (*Phil. Trans.*, 1919, **A**, 218, 35) have observed that several unidentified lines of the ultraviolet spectrum of the sun agree with the ammonia spectrum and hence they have inferred that ammonia is present in the absorbing atmosphere of the sun. The air of manufacturing centres appears to be more rich in ammonia than the air of rural areas, because the consumption of coal sets free ammonia. This ammonia is slowly oxidised to nitrite by oxygen in presence of light.

#### *Summary.*

A. From the following experimental observations it has been deduced that nitrification in soil is more due to photo-oxidation of ammonia and its salts by oxygen of the air at the surface of the soil in presence of sunlight than to the action of bacteria:

(1) Ammonia and its salt solutions are oxidised by air at the ordinary temperature to nitrite in presence of light. This photo-oxidation is markedly accelerated by titania, oxides of zinc and cadmium, magnesia, alumina, silica, etc. Titania is the best photocatalyst obtained so far and it is known that most fertile soils contain titania.

(2) Ammonium salts are oxidised to nitrite when exposed to sunlight after mixing them with sterilized and unsterilized soil. The amount of nitrite formation with the sterilized soil is practically the same as with the unsterilized soil.

(3) The rate of photochemical nitrification is much greater than the rate of bacterial nitrification.

(4) The variation of the nitrate content of the soil in different times of the year follows closely the variation of the total amount of radiant energy received on the earth's surface. In both the Northern

and Southern Hemispheres, the available data show that the nitrate content of the soil and hence the nitrifying capacity of the soil is maximum in the summer and minimum in the winter.

(5) Nitrification in the soil takes place mostly at the soil surface. It appears, therefore, that the nitrification in soil especially in tropical countries, is mainly photochemical in nature.

B. The formation and the occurrence of nitric nitrogen in the atmosphere have been ascribed mainly to the photo-oxidation of ammonia existing in the atmosphere by the oxygen of air in presence of sunlight. This hypothesis explains the following observations: (1) The amount of nitric nitrogen in air is greater at high than at low altitudes. (2) There is a seasonal variation of the nitric nitrogen content of the air, the maximum amount being in the summer and minimum in the winter. (3) The amount of nitric nitrogen in rain water is much greater in tropical countries than in colder countries. (4) The ratio of nitric to ammoniacal nitrogen in the atmosphere in tropical countries is greater than that in colder countries.

We are of opinion that the total amount of nitrites and nitrates received by the earth per acre of soil through rain is greater in tropical than in colder countries.





## The Investigation of Systems with Coarse Particles and its Value for our Knowledge of Colloidal Systems.

By H. FREUNDLICH.

Indian chemists have cultivated colloidal chemistry most remarkably and successfully. It may therefore be opportune to discuss a general problem of colloidal chemistry in a commemoration volume presented to Professor Dr. Sir P. C. Rây, the man to whom the progress of Indian Chemistry owes such a great debt of gratitude.

We are accustomed to consider, as an upper limit of the size of the colloidal particles, a magnitude of about  $500\ \mu\mu$ , which means a state of subdivision, no more visible with an ordinary microscope. It is well known that this limit is conventional, since systems with much coarser particles, up to several  $\mu$  in diameter, also have properties in common with colloidal systems such as Brownian movement, adsorption on their surfaces, etc. Now the investigation of systems with coarser particles has turned out to be of great value for our knowledge of the colloidal state; for many experiments can be much more easily performed with particles of microscopic size than with the much smaller particles of most colloidal systems. I should like to prove this statement by a few examples.

Quite an old example of this kind are Perrin's celebrated experiments on the distribution of particles of suspensions and emulsions under the influence of gravity. With particles of gamboge or mastic having a diameter of about  $1\ \mu$  and more, he was able to make uniform suspensions with an ordinary centrifuge (not an ultracentrifuge) and these produced heights of sedimentation which can be easily determined with an ordinary microscope. Similar experiments with ultramicroscopic particles are much more difficult and have rarely been successful.

A more recent case is the investigation of v. Buza'gh (*Kolloid Z.*, 1929, **47**, 370; 1930, **51**, 105, 230; 1930, **52**, 46; *Naturwiss.*, 1930, **18**, 444) on the adhesion of particles and its importance for

explaining the coagulation of hydrophobic sols. The coagulation of these sols by electrolytes is a phenomenon whose explanation presents many difficulties, although it has been investigated so thoroughly. Before the addition of an electrolyte, the particles having a lively Brownian movement do not adhere to one another even if they touch. The movement does not change after addition of the electrolyte ; but if two particles now come sufficiently close to one another, they stick together and so at last form large clusters which settle down. Now v. Buza'gh has shown, that this phenomenon of adhesion may be investigated more easily and directly with microscopic particles sticking to a wall of the same substance. He generally used particles of quartz and a quartz wall and measured two properties to characterise the adhesion: (1) the *number of adhesion*, by counting the particles first when they have settled on the wall at the bottom of a small vessel and counting them again after having turned the vessel upside down ; (2) the *angle of adhesion*: a cylindrical vessel with the particles covering the wall at its bottom is turned carefully upward and the angle is determined, at which the particles just begin to slide down. The vessel is filled in both cases with pure water or an aqueous solution of an electrolyte.

The strength of adhesion was distinctly correlated to the  $\zeta$ -potential of the particles so long as we have to deal with small concentrations of electrolytes. It may be considered as a rule, that the adhesion is slight as long as the particles have a high  $\zeta$ -potential, while it increases if the  $\zeta$ -potential is lowered. Since the particles of quartz are negative, they are mainly discharged by cations. With a cation of high valency like  $\text{Al}^{+++}$  ion we have an isoelectric point in small concentrations and a positive  $\zeta$ -potential with concentrations only a little higher. The adhesion of the particles accordingly has a strong maximum in the isoelectric point and is lowered again in the region of the positive  $\zeta$ -potential. If we compare solutions with cations of different valency in low concentrations, the  $\zeta$ -potential is lowered parallel to the valency, and we find a rise of adhesion also parallel to the valency.

But the electrokinetic influence is not the only factor that is operative here. In high concentrations the adhesion increases rather independently of the value of the  $\zeta$ -potential. In solutions of salts with univalent inorganic cations like KCl which change the  $\zeta$ -potential of the particles comparatively little, the adhesion is much

stronger than would be expected from the rather high values of the  $\zeta$ -potential.

This behaviour is absolutely parallel to that of the coagulation of negative hydrophobic sols, a strong adhesion of the particles to one another always lowering the stability of the sols. The coagulation is first correlated to the  $\zeta$ -potential: thus we have minimum stability in the isoelectric point, and renewed stability in somewhat higher concentrations of cations which are able to reverse the charge of the particles due to the influence of the valency of the cations (Schulze-Hardy rule). On the other hand an influence which cannot be regarded as electrokinetic, is observed, for instance, in the case of the coagulation of negative sols with salts like KCl in concentrations in which the  $\zeta$ -potential is much higher than the critical potential which generally has to be reached to cause coagulation (Powis, *Z. Phys. Chem.*, 1915, **89**, 186). We thus see that the laws of adhesion as found with coarser particles, hold good also for the coagulation of the small particles in colloidal solutions. It is in excellent agreement with the views of v. Buza'gh, who has shown that small particles of quartz, but of microscopic visibility, show a very small number of adhesion in pure water, they being torn from the wall by the Brownian movement. Ultramicroscopic particles, therefore, ought to show no tendency to stick to one another in pure water. This is indeed the case, for, before the addition of the electrolyte, the colloidal solutions are stable.

The forces influencing the adhesion itself are not yet sufficiently known. We have repelling and attracting forces. The repelling ones are most likely caused by the electric charge of the particles; the attracting ones are perhaps of the same kind as those assumed in the theory of van der Waals.

Closely connected to the question of adhesion is the phenomenon of thixotropy, that is, the isothermal sol—gel transformation; concentrated sols congeal to a jelly and can be liquefied by shaking, a transformation which may be repeated over and over again. Thixotropy is not only found in true sols, but also in suspensions with coarser particles, for instance in aqueous suspensions of bentonite (Freundlich and Sachs, *Kolloid Z.*, 1928, **46**, 290; Buza'gh, *ibid.*, 1928, **47**, 228; Hauser, *ibid.*, 1929, **48**, 5). Its particles are to a high percentage not truly colloidal, they being needle-shaped and of microscopic magnitude in one dimension. Bentonite is a clay-like substance always containing a certain

amount of alkali metals. If we remove these by electrodialysis, the suspensions are no more thixotropic, but they regain this property as soon as we add some alkali salt or alkali hydroxyde to the suspension. According to Hauser (*Kolloid Z.*, 1929, **48**, 5) this behaviour may be investigated with the ultramicroscope in pretty dilute suspensions. Before the addition of the electrolyte to a suspension of electro dialysed bentonite, the particles show a lively Brownian movement. If increasing amounts of electrolytes are added carefully enough, it may be seen, how first the translatory component of the movement disappears and then the rotatory component, the particles lying distinctly separated from one another without moving in the thixotropic gel. If this is liquefied again by shaking carefully, the rotatory component reappears first with the translatory motion afterwards. So the investigation of these larger particles reveals important features of the thixotropic behaviour, hardly to be recognised in sols and gels with smaller particles.

The state of aggregation and the shape of particles may also sometimes be cleared up more easily with coarser particles. We have the well known case of latex (Freundlich and Hauser, "Zsigmondy-Festschrift, Ergänzungsband" 1; *Kolloid Z.*, 1925, **36**, 15; Hauser, *Kolloid Z.*, 1930, **53**, 78). It contains particles of widely different magnitudes, some up to  $5\ \mu$  in diameter. These may be treated with a micro-dissection needle or a micropipette under the ordinary microscope with the result, that the particles are shown to be built up of a more fluid interior enclosed in a stiff skin. The skin seems to consist partly of a more highly polymerised hydrocarbon, and partly of proteins. This complicated structure of the particles also explains their extraordinary pear-like shape.

In all cases discussed so far, we drew conclusions from the behaviour of systems with coarser particles; we are able to consider them as very similar to that of colloidal systems. It may be remarked finally, that the investigation of coarser particles may be of value for solving questions of colloidal chemistry in quite a different way. The volume of sedimentation of such particles is a characteristic property depending especially upon their shape, their  $\zeta$ -potential and their hydration (Ostwald and Haller, *Koll.-Chem. Beih.*, 1929, **29**, 354; Buza'gh, *ibid.*, 1930, **32**, 114). We are often able to distinguish between these different possibilities. If we coat such coarse particles (of quartz or iron-oxide) with hydrophilic colloids (gelatin and other proteins, etc.) and then examine the volume of

sedimentation, important properties of the hydrophilic colloids may be revealed. For instance particles of quartz coated with egg-albumin or gelatin show a distinct maximum of the volume of sedimentation at the isoelectric point. This proves that the  $\zeta$ -potential is instrumental and not the hydration of the proteins (Freundlich and Lindau, *Biochem. Z.*, 1931, 234, 170).

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## Study of Inorganic Jellies.

By SATYA PRAKASH.

The study of such inorganic jellies as silicic and titanlic acids and alumina takes us back to the days of Rose, Berzelius, Crum and Graham, but it is only for the last few years, that the subject has met with the proper scientific attention. The discovery of various hydroxide jellies, as of iron, chromium, aluminium, tin and copper by Grimaux, Schalek and Szegvary, Reinitzer, Bunce and Finch and Weiser gave a fresh impetus to the study of the subject. Coloriano, Deiss, Klemp and Gyulai, and Holmes and his co-workers made valuable contributions to the preparation of arsenate and phosphate jellies of zinc, manganese, iron and chromium. Here a reference may also be made to the work of various investigators on the beautiful jellies of zirconium hydroxide, ceric hydroxide and vanadium pentoxide.

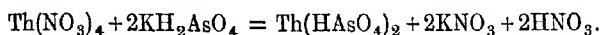
In some of the publications from these laboratories the author (Prakash and Dhar, *J. Indian Chem. Soc.*, 1929, **6**, 587; 1930, **7**, 367, 691) has described details of the preparation of numerous new inorganic jellies. The following jellies have been for the first time obtained in this laboratory : thorium arsenate, thorium molybdate, thorium phosphate, zirconium borate, zirconium molybdate, ferric tungstate, ferric molybdate, ferric borate, chromic tungstate, stannic arsenate, stannic phosphate, stannic tungstate, stannic borate, stannic molybdate, ceric arsenate and ceric borate. Modified methods for the preparation of iron, chromium, aluminium, tin and zirconium hydroxide jellies have also been proposed. Some of the jellies have been prepared by metathetical reactions under suitable conditions and concentrations, while other jellies have been obtained by preparing their sols of proper concentrations and dialysing and finally coagulating them with necessary amounts of electrolytes.

In spite of the fact that every jelly requires a special treatment and is only formed under restricted conditions, some generalities can also be observed. Whenever the jellies are obtained by metathetical



reactions, as in the case of arsenate, phosphate and molybdate jellies of thorium, the process is completed in the following two steps:

1. Formation of the colloidal phase of sufficient concentration. The precipitate obtained metathetically is peptised by the adsorption of similarly charged ions. For example, in the case of thorium arsenate jelly, the metathetical reaction may be represented as follows:



The amount of thorium nitrate taken for the formation of this jelly is always present in much excess to what is necessary for the above stoichiometric equation. The insoluble thorium arsenate undergoes peptisation by the adsorption of thorium ions as well as hydrogen ions from the system, and thus, a stable colloidal phase is formed.

2. When the colloidal phase of suitable concentration has been formed, the second step consists in the coagulation of it by the adsorption of oppositely charged ions. The process of jelly formation is essentially a coagulation process, with the difference that in this special case, as coagulation proceeds on, the solvent or dispersion *medium* is also being continuously imbibed by the coagulum, so much so that in the end a solid mass is obtained.

In some cases, the colloidal systems obtained metathetically are not sufficiently pure as to give suitable jellies and in such cases, it becomes necessary to purify them by the process of dialysis. If the dialysis is continued for a suitable period, and if the sol is of sufficient concentration, the sol may spontaneously set to a jelly either during the process of dialysis, or on allowing the dialysed sol to age. In the case of slightly less purified sols, the jellies are obtained by coagulating it with suitable concentrations of electrolytes. Thus ferric arsenate sol is obtained metathetically by adding potassium arsenate to excess of ferric chloride solution, whereby the sol is stabilised by the adsorption of ferric, hydrogen and other positively charged ions. If the sol without dialysis is coagulated by strong concentrations of potassium sulphate, the coagulum obtained is a white opaque heavy mass which on allowing to stand settles down as a precipitate. However, if the sol is dialysed for a sufficient time, the coagulum obtained by adding potassium chloride or sulphate is quite transparent and gelatinous, and under suitable concentrations it gives rise to transparent and stable jellies.

The failure to obtain jellies of vanadates, antimonates and similar other salts of polybasic acids is partly due to the fact that their salts with heavy metallic ions are not capable of being peptised to a marked extent by positively charged ions. Their sols of low concentrations are precipitated during the course of dialysis. The formation of jellies appears to be also a characteristic intrinsic property of the metallic as well as acid ions. For example, thorium salts easily give jellies with arsenate, molybdate and phosphate alkali salts, but the attempts to prepare its tungstate jelly has been so far unsuccessful. Manganese and zinc salts give arsenate jellies very readily but their phosphate, molybdate, tungstate or borate jellies have not yet been prepared. Similarly, the author's attempts to prepare the corresponding jellies of mercury, cobalt, nickel and cadmium have not given any fruitful results. In spite of the fact that in some cases the coagulum obtained is highly gelatinous, the system could not yield jellies of stable texture.

In numerous publications from these laboratories, we (Prakash and Dhar, *J. Indian Chem. Soc.*, 1929, **6**, 391; 1930, **7**, 367, 417, 591; Prakash, *Z. anorg. Chem.*, 1931, **201**, 301; *J. Soc. Chem. Ind.*, 1931, **50**, 387) have been studying all sorts of inorganic jellies, ranging from transparent to perfectly opaque, and from stable to loose ones, and have also investigated the mechanism of their formation. The formation of a jelly consists in the transformation of a liquid phase to a solid without any marked change in volume and temperature, and possibly there is no change in the electric conductivity too, during the course of gelation. In the case of very transparent jellies, there is no appreciable change in extinction coefficients. In some jellies, marked increase in the extent of light scattering has been observed. In some cases the hydrogen ion concentration appears to be diminishing to the extent of  $50 \pm 10\%$  for sometime in the beginning, and then at a later stage, an asymptotic limit is reached and during the formation of actual structure of the jelly, the hydrogen ion concentration remains constant. Only a few jellies like vanadium pentoxide have been found to be doubly refractive. In view of these facts, jelly formation appears to be a very complicated phenomenon.

Various mechanisms of jelly formation have been proposed by von Weimarn ("*Grundzuge der Dispersoid Chemie*", 1911, 39; *J. Russ. Phys. Chem. Soc.*, 1915, **47**, 2163), Bradford (*Biochem. J.*, 1918, **12**, 351; 1921, **15**, 553), Kraemer (*J. Phys. Chem.*, 1925, **29**, 1523), Weiser (*J. Phys. Chem.*, 1924, **28**, 26), Arsem (*J. Phys. Chem.*, 1926,

30, 306) and various other investigators. From his extensive researches on the nature of precipitates, von Weimarn has been led to think that a precipitate may be crystalline, amorphous or gelatinous according to the conditions of formation. In view of the amount of supersaturation or the degree of specific saturation, five stages are distinguished. In the first stage for slight supersaturation, no precipitation occurs and colloidal solutions are formed. In the second stage with higher supersaturation, perfect crystals are obtained in a relatively short time; in the third stage, skeleton crystals and needles are obtained. When the fourth stage is reached a curdy, apparently amorphous, precipitate is obtained; and in the highest stage of supersaturation, a jelly is formed.

Bradford also supports Weimarn's views and regards that gels should comprise two phases, an ultramicroscopic solid phase bathed in a liquid dispersion medium from which it has crystallised out and which it retains partly by molecular and partly by capillary forces.

Von Weimarn's views have been criticised by Bancroft (*J. Phys. Chem.*, 1920, **24**, 100), who thinks that while it is apparently true that one can get any salt coming down in a gelatinous form if the concentrations of reactants are sufficiently high, but these are not the conditions under which jellies are usually obtained. In some cases it has also been shown that the precipitate obtained metathetically could have developed considerable supersaturation, yet the jelly was not formed.

Weiser's view that uniform slow coagulation results in the formation of jellies is also not satisfactory. No doubt, uniform slow coagulation helps in the development of fine texture, yet it cannot be essentially regarded as a condition for the formation of a jelly. Some of the jellies are formed within only a few seconds where even it is difficult to assume that the contents have been mixed uniformly and thoroughly.

Kraemer regards the gel formation as the result of an incomplete or unsuccessful attempt at precipitation of a solid phase from a liquid system. Thus metathetical reactions, which are expected to yield solid insoluble products, may result in the gel formation, or a change in solvent may cause a solute to precipitate out in the form of a gel, or a gel may be formed by the coagulation of a sol. Arsem says that in many cases when a substance separates out from solution, conditions do not favour the building of a normal and regular crystalline lattice structure, specially when the substance has a high

molecular weight or great complexity; or when the solution from which it separates is greatly supersaturated. In many cases the gels are obtained only because their large unsymmetrical units do not orient themselves, regularly upon separation from solution, so that an expanded lattice is built up with its units irregularly arranged and not closely packed. Thus according to Arsem, regular orientation of particles gives rise to crystals and whenever this is prevented by the velocity of the separation of solute, a gel is expected.

Smoluchowski (*Z. Phys. Chem.*, 1917, **92**, 129) has assumed that a sphere of attraction exists around each particle such that any other particle entering this sphere will be held in it. And thus from primary particles, double, triple and multiple particles are formed. In our hypothesis of jelly formation, we have assumed that the sphere of attraction existing around the primary particle is not only capable of holding statically any other primary particle, but it is also capable of binding up the dispersion medium. When a primary particle is surrounded by a Helmholtz layer of charge, as in the case of colloidal solutions, the forces of attraction remain latent and are not allowed to operate. As the charge is gradually neutralised, these forces become active and then they may cause agglomeration according to Smoluchowski or may begin to imbibe layers after layers of solvent and thus develop hydration. The nature of the coagulum thus depends upon the two tendencies of the particles, one the hydration tendency and the other the agglomeration tendency. In the case of wellknown lyophobic sols, the agglomeration tendency predominates over the hydration and an anhydrous coagulum is obtained on the neutralisation of charge. Where the hydration tendency is the most predominant, transparent jellies are obtained. Where the two tendencies are in balance, either opaque jellies are obtained or such jellies are obtained which may readily undergo syneresis.

There are some complications about the nature of hydration itself. Water may be bound up in a jelly in three forms according to von Weimarn (*Rep. Imp. Ind. Res. Inst. Osaka*, 1928, **9**, 1): interatomic hydration, surface hydration and structure hydration. From the times of van Bemmelen (*Rec. trav. Chim.*, 1888, **7**, 37) various investigators have been trying to obtain a quantitative idea of the atomic hydration, i.e., water in crystal hydrates in the case of various gels as alumina, silica, etc., but the results are very uncertain. In a jelly system, most of the water appears to be in the state of surface hydration, and the rest may be

assumed to be mechanically imbibed in the structure of the jelly. Our ordinary knowledge of surface adsorption does not take us very far when the forces governing surface hydration are considered. In some of the jellies, as much as two to three hundred molecules of water appear to be associated with a molecule of solid substratum, and this cannot be accounted for by mere surface phenomenon, until multimolecular layers of water be supposed to be associated with the surface of the colloid.

In a recent communication, the author (*Kolloid Z.* 1932, **60**, 184) has made an attempt to have a quantitative idea of superficially and structurally bound water in inorganic jellies from viscosity measurements. The author has shown that during the course of jelly formation, the viscosity results show three distinct stages. In the first stage, which is exhibited in the case of metathetically produced jellies, there is very little change in the viscosity with time, whilst in the second stage, the viscosity exponentially increases with time. The author has assumed that this stage corresponds to where the jelly-forming units are developing surface hydration. In the third stage, the viscosity changes are very abrupt and irregular, a stage which corresponds to the structural viscosity. By the use of Hatschek's expression, the structural and surface hydrations have been calculated out. It has been shown that ordinarily a jelly contains as much as  $70 \pm 10\%$  of water as surface hydration, the actual figures varying from jelly to jelly.

The phenomenon of syneresis is directly connected with the amount of structurally imbibed water. In a previous publication on syneresis (*J. Indian Chem. Soc.*, 1930, **7**, 417) the influence of the concentration of electrolytes on the extent of syneresis has been investigated. It has been shown that the amount of coagulating electrolytes added to a jelly-forming sol controls not only the nature of the jelly, but also the extent of syneresis. There is always a fixed minimum of the coagulating electrolyte necessary to give a stable jelly, and any amount greater than that brings about the further agglomeration of particles which is either exhibited in the increased opalescence of the jelly or in other cases, in the shrinkage of the network. During the shrinkage of the network, the structurally imbibed liquid is squeezed out. This phenomenon is known as syneresis. The greater the concentration of coagulating electrolyte, the less is the time for the formation of a jelly, and in such cases, the greater would be the amount of water imbibed structurally, and so the

amount of syneresis would be greater. The addition of large amounts of electrolytes gives only a gelatinous precipitate, and not a jelly because in that case, the agglomeration tendency of the particles predominates over the hydration tendency. The maximum syneresis in the case of jellies has been observed to be about 30% of the total volume and this also shows that in a jelly the major amount of water present is superficially hydrated.

In one communication (*J. Phys. Chem.*, 1932, **36**, 2483) the author has made detailed investigations on the variations of extinction coefficients during the course of jelly formation. According to transparency the jellies may be divided into three classes: (1) Perfectly transparent sols giving rise to perfectly transparent jellies without any change in the extinction coefficients; (2) transparent sols yielding jellies only slightly opalescent at the point of setting, but their opacity increasing with time. (3) Transparent sols developing opalescence, and by the time of setting to a jelly becoming perfectly opaque. The opalescence of a jelly depends not only on the purity of the sol but on the temperature of coagulation, the concentration of coagulating electrolyte and on the nature of ions bringing about the coagulation. Impure sols generally give opaque coagulum. One and the same sol can under different conditions give jellies of varying transparency according to whether the conditions favour the development of hydration tendency or the agglomeration tendency.

The nature of a jelly, and especially its setting time can be markedly varied by allowing it to set in the presence of various organic substances. In a publication, the author (*Z. anorg. Chem.*, 1931, **201**, 301) has studied the influence of glycerine, glyccoll, cane sugar and urea on the setting of arsenate, phosphate and molybdate jellies of thorium. The influence of these peptising and sensitising substances on jelly-formation is essentially the same as on coagulation. The jellies are more readily obtained in the presence of urea while the time of setting is increased in presence of cane sugar, or glycerine. Possibly the extent of hydration is also influenced in the presence of these substances.

Our results on the thixotropic behaviour of thorium jellies (*J. Indian Chem. Soc.*, 1931, **8**, 549) also support the agglomeration hydration hypothesis advanced by the author to explain the mechanism of jelly formation. It has been stated that on shaking, the structurally imbibed liquid of a jelly is set free forming a dispersion medium for the jelly forming elements, and thus the thixotropic

jellies are transformed to the sol condition. The structure is, however, again developed and the jelly is formed. By comparing the original time of setting and the thixotropic time of setting, a rough idea can be had of the amount of water superficially and structurally bound.

We are of the opinion that the formation of organic jellies as starch, gelatin, agar agar, pectin, dyestuffs, soaps, etc., is also guided by the two factors, agglomeration and hydration. Ordinarily, these jellies appear to differ from inorganic jellies in the following respects. These substances exhibit a higher tendency to adsorb stabilising ions. They can take up any charge according to the medium; thus both on the acid side and on the alkaline side the charge on them is increased. In the case of inorganic jellies, the time of setting is generally decreased as the temperature is increased, (Prakash, *J. Indian Chem. Soc.*, 1932, 9, 193) because the coagulation is more rapidly effected at higher temperatures. In the case of organic jellies, lowering of the temperature favours jelly formation. It appears that at higher temperatures, the substances exist in more or less molecular conditions. As the temperature is lowered, due to the decrease of solubility, the particles begin to aggregate and the colloidal phase is formed. Another important difference between the organic and inorganic jellies is the heat reversibility. Inorganic jellies once dried do not generally take up water again and do not swell, whilst gelatin, starch, etc., can reform jellies after being dried once. The phenomenon of swelling is also markedly exhibited in them. This is probably due to the fact that inorganic substances rapidly undergo ageing and that the surface energy is markedly decreased when once they are dehydrated.

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**Studies on Proteolytic Enzymes in Plants.**  
**The Proteolytic Enzyme in the Milky Juice of**  
***Calotropis Gigantia* (Akanda).**

BY KALI PADA BASU AND MADHAB CHANDRA NATH.

The first systematic investigation on the proteolytic enzymes in plants we owe to the botanist S. H. Vines (*Ann. Bot.*, 1902, **16**, 1 and later papers, also "The Proteases of Plants," London, 1930). Although Vines had paid no attention to keep the  $pH$  values constant and employed only qualitative methods to determine the action of enzymes, his results deserve attention. According to Vines there are two proteases in plants: (1) the peptase that splits protein molecules to peptones, and (2) the ereptase that hydrolyses the peptones formed to the stage of amino-acids. Plant-trypsin should, according to Vines, be considered as a mixture of the peptase and ereptase.

Dernby in his investigations on the proteases of yeast (*Biochem. Z.*, 1917, **81**, 107), and Lundin in his work on the malt proteases employed more modern methods. Dernby found three proteolytic enzymes in yeast: (1) yeast-pepsin that acts at an optimum  $pH$  of 4.5, (2) yeast-tryptase with a  $pH$  optimum at 7.0, and (3) yeast ereptase, similar in properties to the erepsin of the intestine with  $pH$  optimum at 7.8.

The nature and number of proteolytic enzymes of plants have been thoroughly elucidated by the experiments of Willstätter and Grassmann on the proteases of *Carica papaya* (Hoppe-Seyler, 1924, **138**, 184, and later papers) and of the yeast (Hoppe-Seyler, 1926, **153**, 250 and later papers) and specially by the recent investigations of Grassmann and his students (Hoppe-Seyler, 1927, **167**, 188, 202; 1928, **175**, 18; 1930, **186**, 183; 1931, **194**, 124). They have succeeded in obtaining very pure and active specimens of enzymes, free from most of the accompanying impurities. They have also resolved the enzyme mixtures into their components. In the milky juice of *Carica papaya* which had been previously investigated by Vines, they found



an enzyme, papain, which hydrolysed gelatine, fibrin and other similar complex proteins. It attacked peptone only when activated with substances like hydrocyanic acid and sulphuretted hydrogen. The pH optimum was found at about 5 and the activity fell rapidly in more acid regions. From autolysate of yeast-cells, Grassmann and his students have isolated the following enzymes: (1) proteinase with a pH optimum at pH 5, which is probably identical with papain, (2) amino-polypeptidase, pH optimum between 6.7 and 7.0, (3) dipeptidase pH optimum at 8.0, and (4) also traces of carboxy-polypeptidase.

In his investigation on the proteases of animal origin Waldschmidt-Leitz (*Hoppe-Seyler*, 1927, **167**, 285; 1930, **188**, 17), has resolved the trypsin into proteinase and carboxypolypeptidase and the erepsin into amino-polypeptidase and dipeptidase and these constituent enzymes have been shown to be identical with those obtained from plants. The analogues of plant-proteolytic enzymes are to be sought not in the proteases of the digestive system of higher animals but rather in lower animals and in organs and tissues of the higher animals not connected with digestion *e.g.*, in spleen, liver, kidney and in white blood corpuscles (Waldschmidt-Leitz, *loc. cit.*; Willstätter and Baman, *Hoppe-Seyler*, 1928-29, **180**, 127; 1929, **185**, 267).

Investigation on plant proteases have not been too numerous and it was thought that investigations of some plants of this country and their secretions with regard to their content of proteases might yield interesting results. We have chosen as the subject matter of investigation the milky juice of *Calotropis Gigantia* which is known in this country as *Akanda* and which is supposed to have some medicinal properties.

#### EXPERIMENTAL.

The milky juice was collected in sterile vessels after breaking the twigs and always preserved in an ice chamber. The proteolytic activity was tried upon the following substrates: gelatine, casein, egg-albumin, fibrin and peptone (Witte). The pH of the reaction mixture was kept constant with citrate buffers. The extent of hydrolysis which always limits itself to breaking a -CO-NH- bond with production of a free amino and carboxyl group, was followed by the method of Willstätter. This consisted in titrating a known volume of the mixture in 90% alcoholic solution with about N/25-KOH solution in 90 p.c. alcohol with thymolphthalein as the indicator.

A 5 p.c. stock solution of gelatine was prepared. The gelatine was previously purified according to method of Loeb (*Die Eiweisskörper*, p 39, Berlin 1924). This consisted in treating 50 g. of gelatine with 3 litres of  $M/128$  acetic acid at  $10^\circ$  stirring frequently and allowing the mixture to stand for half an hour. Supernatant liquid was then decanted off and the process was repeated. The acid was then replaced by an equal volume of distilled water at  $5^\circ$  and the gelatine was then filtered and washed on a Buchner funnel five times, each time with 1 litre of water at  $5^\circ$ . The gelatine was then heated to  $50^\circ$  when it melted and was diluted to the required volume.

A 2 p.c. solution of casein was prepared by dissolving 2 g. of pure casein (according to Hammarsten) in 100 c. c. of  $N/20$  NaOH. It was brought to the desired  $p_H$  by adding  $N/2$ -HCl in drops.

2 P. c. solutions of Merck's egg-albumin and witte peptone were also prepared.

All these stock solutions were preserved with the addition of a few drops of toluene.

The extent of hydrolysis was measured in 25 c.c. measuring flasks. 10 C.c. of the substrate solution were brought up to the desired  $p_H$  with the addition of HCl or NaOH in drops. Clark and Lubs's series of indicators for the determination of  $p_H$  were used for this purpose. 1 C.c. of the citrate buffer and 1 c.c. of the milky juice were then added and the mixture diluted to 25 c.c. and a drop of toluene added. All these solutions were previously heated to  $40^\circ$  and the reaction carried out in a thermostat maintained at  $40^\circ$ . 5 C.c. were withdrawn from time to time and titrated with standard alcoholic KOH (about  $N/25$ ), by means of a micro-burette.

Blank experiments showed that the substrates alone underwent no appreciable hydrolysis between the range of  $p_H$  investigated ( $p_H$  2.7). The following tables indicate the results obtained. The different samples of juice are marked A, B, C, etc.

TABLE I.

Substrate, gelatine.			Sample of juice (A).			Temp. $40^\circ$ .	
$p_H$	...	...	... 5.96	5.31	4.95	4.44	3.94
Hydrolysis after 1 hr. (c.c., $0.04N$ -KOH)			0.57	0.89	0.93	0.67	0.0
Hydrolysis after 3 hr. (c.c., $0.04N$ -KOH)			0.86	1.41	1.63	0.78	0.0

TABLE II.

		Substrate, casein.			Sample (A).			Temp. 40°.		
pH	...	...	9.10	6.67	5.96	5.31	4.95	3.94	3.36	2.97
Hydrolysis after 1 hour										
(c.c., 0.04N-KOH)	...	0.0	0.23	0.38	0.44	0.85	0.25	0.04	0.0	
Hydrolysis after 3 hours										
(c.c., 0.04N-KOH)	...	0.0	0.37	0.51	0.78	1.11	0.61	0.14	0.0	

At pH 4.44 no experiment could be done; this being the isoelectric point of casein, at this pH the substrate came out of the solution.

TABLE III.

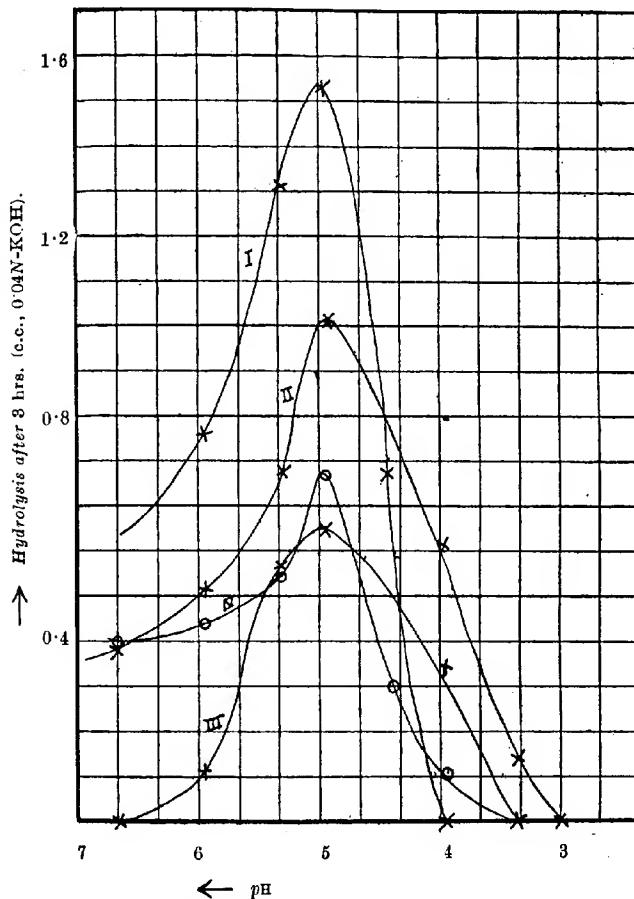
		Substrate, fibrin.			Sample of juice (A).			Temp. 40°		
pH	...	...	9.10	6.67	5.96	5.31	4.95	3.94	3.36	
Hydrolysis after 1 hour										
(c.c., 0.04N-KOH)	...	0.0	0.0	0.03	0.33	0.48	0.28	0.28	0.0	
Hydrolysis after 3 hours										
(c.c., 0.04N-KOH)	...	0.0	0.0	0.11	0.56	0.65	0.35	0.0		

TABLE IV.

		Substrate, egg-albumin.			Sample of juice (B).			Temp. 40°		
pH	...	...	6.67	5.96	5.31	4.95	4.44	3.94	3.36	
Hydrolysis after 1 hour										
(c.c., 0.04N-KOH)	...	0.22	0.42	0.40	0.49	0.17	0.04	0.0		
Hydrolysis after 3 hours										
(c.c., 0.04N-KOH)	...	0.40	0.44	0.54	0.77	0.30	0.10	0.0		

Fig. I represents all these results graphically.

FIG. 1<sub>c</sub>



Curve I, Gelatin ; Curve II, Casein ; Curve III, Fibrin ; Curve IV, Egg-albumin.

Witte's peptone underwent no hydrolysis. It thus appears that in this juice we are dealing with a protease that is very much akin to, if not identical with the papain. There is one important difference however. Willstätter and Grassmann found that for papain the optimum pH was identical with the isoelectric point of the protein. Thus they found that papain hydrolysed gelatine most readily at pH 5 and fibrin at pH 7.2 and isoelectric points of gelatine and

fibrin are at  $pH$  4.8 and 7.2 respectively. But according to our experiments it is quite clear that the  $pH$  optimum for the proteolytic enzyme in the milky juice of *Calotropis Gigantia* is at  $pH$  5 independent of the nature of the protein. It is interesting to note that the milky juice itself is acid and has got a  $pH$  value in the neighbourhood of 5. It might also be mentioned that the milky juice when preserved in the refrigerator keeps its proteolytic activity unimpaired for weeks. But when the juice is dried in vacuum at the ordinary temperature, the residue has very little action towards the proteins.

*Effect of Temperature.*—We have also determined the temperature at which this enzymic hydrolysis proceeds most rapidly. The determinations were made at the optimum  $pH$ , viz.,  $pH$ , 4.95. Table V indicates the results.

TABLE V.  
Sample of Juice (B). Strength of KOH, 0.0325N.

Substrate	Temp. 30°.		Temp. 40°.		Temp. 50°.		Temp. 60°.		Temp. 70°.	
	Hydrolysis after 1 hr.	3 hrs.	Hydrolysis after 1 hr.	3 hrs.	Hydrolysis after 1 hr.	3 hrs.	Hydrolysis after 1 hr.	3 hrs.	Hydrolysis after 1 hr.	3 hrs.
Gelatine	0.90 c.c.	1.34 c.c.	0.92 c.c.	1.44 c.c.	1.01 c.c.	1.56 c.c.	0.43 c.c.	0.54 c.c.	0.0 c.c.	0.0 c.c.
Casein	0.80	1.06	0.82	1.04	0.85	1.15	0.83	0.98	0.0	0.0
Egg-albumin	0.38	0.65	0.42	0.68	0.42	0.53	0.42	0.63	0.0	0.0
Fibrin	0.15	0.23	0.26	0.33	0.34	0.43	0.32	0.39	0.0	0.0

It would thus appear that 50°C is the temperature at which the enzyme acts most rapidly except for the substrate egg-albumin for which 40° appears to be the optimum temp. At 70° the enzyme is completely destroyed. In this respect also there seems to be a difference between this enzyme and the papain which exerts its influence most quickly at higher temperatures, viz., between 65-70° (Hoppe-Seyler, 1924, 138, 184).

*Activation of the enzyme.*—Papain when previously activated with HCN, or H<sub>2</sub>S can hydrolyse peptone. Similar activation has also been observed in the case of yeast proteinase and also in the case of kathepsin, the analogue of papain in the animal kingdom which has been isolated from kidney, spleen and white blood corpuscles. This phenomenon of activation has been most thoroughly investigated by Grassmann and his students for plant proteases (Hoppe-Seyler, 1930, 186, 183; 1931, 194, 124) and by Waldschmidt-Leitz and his students for proteases of animal origin (*Naturwiss.*, 1930, 18, 644). They hold that glutathion which has been shown to be a constituent of many plant and animal cells, is, in its reduced form, responsible for this activation.

To carry out the hydrolysis of the proteins by the enzyme in presence of an activator, we kept 1 c.c. of the milky juice with the buffer-solution and the activating solution in the thermostat for about an hour and then added the substrate. The measurements were all carried out at pH 4.95. The temperature was kept at 40°. The activators tried were H<sub>2</sub>S, HCN, cystein hydrochloride, and cystin. As HCl or NaOH solutions were used to bring the substrate solutions to the desired pH it was first ascertained that NaCl has got no influence on the rate and extent of hydrolysis. The enzyme did not hydrolyse the peptone in the presence of any of the activators. In this respect it differs from papain.

With regard to its behaviour towards complex proteins in presence of an activator we found a very interesting result. With juice collected from young and green plants the initial activity was already high and the amount of activation small. With juice collected from older plants, the initial activity was very low and the amount of activation high, final amount of hydrolysis in both cases being almost the same.

TABLE VI.

Substrate, gelatine.  $pH = 4.95$ . Sample of juice (C) (from green plants). Temp.  $40^{\circ}$ .

Activator.	Hydrolysis (0.031N-KOH in c.c.).	
	after 1 hour.	after 3 hrs.
—	0.88	1.13
H <sub>2</sub> S	1.08	1.64
Cystein (0.04M)	1.18	1.62

TABLE VII.

Sample of juice (D) (from older plants).  $pH = 4.95^{\circ}$ . Temp.  $40^{\circ}$

Activator.	Gelatine		Casein	
	Hydrolysis (c.c., 0.0313 N-KOH)		Hydrolysis (c.c., 0.0313N-KOH)	
	after 1 hr.	after 3 hrs.	after 1 hr.	after 3 hrs.
—	0.10	0.15	0.05	0.10
H <sub>2</sub> S	1.2	1.65	0.68	1.14
HCN (0.022M)	1.0	1.3	0.72	1.2
Cystein (0.04M)	1.06	1.31		
Cystin (0.04M)	0.17	0.27		

It will thus be clear from Table VII that H<sub>2</sub>S, HCN, and cystein all activate the enzyme but cystin is without any action. The juice from green plants appears to possess a natural activator which is probably changed in some way as the plant grows older and causes the proteolytic activity of the juice to diminish. The dry residue from juice shows the presence of organic sulphur. This fact and the observation that cystein and not cystin acts as an activator for the enzyme seems to indicate that in the juice of green plants an organic compound like glutathion is present in the sulphydryl (SH) form which acts as a natural activator. With the ageing of the plant the sulphydryl compound is probably converted into the disulphide form and is unable to activate the proteolytic enzyme. We are at present trying to isolate this sulphur compound from the milky juice.



Attempts have been made to formulate a connection between respiration and protein-hydrolysis in animal cells from the phenomenon of activation of proteolytic enzymes like kathepsin by sulphhydryl compounds (Grassmann, *Hoppe-Seyler*, 1931, 194, 128).

It is generally assumed that the phenomenon of activation of enzymes is due to the formation of a complex between the activator and the enzyme (*Hoppe-Seyler*, 1924, 138, 186). But Myrback (*Hoppe-Seyler*, 1926, 158, 160) and recently Krebs (*Biochem. Z.*, 1930, 220, 189) suggest that the action of these activators consists in forming a complex with traces of metals, which are present in the enzyme preparations and which inhibit the action of the enzyme. It is of course well known that substances like HCN,  $H_2S$  and cystein can form complexes with metallic ions specially with iron salts. Some recent experiments of Grassmann (*Dissertation, Schoenebeck, München*, 1930) show that the amounts of metals found by Krebs in enzyme preparations appear to be too high. Moreover, it is well known that pyrophosphates that are widely distributed in animal and vegetable organisms (*Naturwiss.*, 1928, 16, 298; *Biochem. Z.*, 1928, 202, 466; 203, 154), are also capable of forming complexes with metals and should, in case metals have a poisonous effect, act as activator of the enzyme. We have carried out some experiments with sodium pyrophosphate. Table VIII indicates the results. The juice with the buffer solution and pyrophosphate was kept at  $40^\circ$  for an hour before the substrate was added.

TABLE VIII.

Substrate, gelatine.  $pH=4.95$ . Temp.  $40^\circ$ . Sample of juice (C).

Conc. of sodium pyrophosphate Mol./litre.	Hydrolysis (c.c., 0.037N-KOH)	
	after 1 hr.	after 3 hrs.
0.0008	0.35	0.48
0.004	0.07	0.12
0.004 ( $H_2S$ also present)	1.25	1.63

It will be seen that pyrophosphate inhibits the action of the enzyme. But if  $H_2S$  is also present, we get the usual activation and pyrophosphate is without any action. This observation makes the theory of activation of the enzyme through complex formation with the poisonous metal ion, very improbable.

*Summary.*

1. The milky juice of *Calotropis Gigantia* (*Akanda*) contains a proteolytic enzyme that is similar in some respects to papain and can hydrolyse gelatine, casein, egg-albumin and fibrin but not peptone.
2. The optimum  $pH=4.95$  and the optimum temperature is  $50^{\circ}$ .
3.  $HCN$ ,  $H_2S$  and cystein are capable of activating the enzyme. Cystin is without action.
4. Pyrophosphate inhibits the action of the enzyme. But if an activator like  $H_2S$  is also present, pyrophosphate is without any action.
5. Even in the presence of an activator the enzyme is incapable of hydrolysing peptone.
6. A sulphur compound is present in the milky juice which in its sulphydryl form is probably responsible for the activation.

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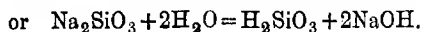
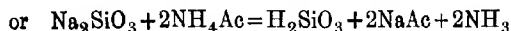
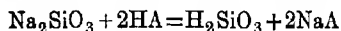


## Gelation of Silicic Acid.

By MATA PRASAD

Gels are usually obtained by the slow coagulation of colloidal solutions provided there is a sufficient concentration of the colloid and the colloidal particles are hydrophilic in nature. Silicic acid is a substance which gets highly hydrated and if a silicic acid sol is allowed to coagulate slowly, a silicic acid gel is easily obtained. These gels first prepared by Graham<sup>1</sup> can be prepared by mixing solutions of sodium silicate with those of organic and inorganic acids.<sup>2,3</sup> Bhatnagar and Mathur<sup>4</sup> have, however, prepared them by mixing a 12.5 per cent solution of sodium silicate with a 10 per cent solution of ammonium acetate.

In all these methods silicic acid is first formed in the molecular state (*cf.* Mylius and Groschoff<sup>5</sup>) according to the following reactions:



The possibility of the first two reactions is supported by the fact that the crystals of the sodium salts of the acids grow in the form of needles when the gel is allowed to dry (*cf.* Fells and Firth<sup>6</sup>). Also a large amount of ammonia is evolved when ammonium acetate is used for the formation of the gels.

The crystalloidal silicic acid rapidly polymerises and goes over to the colloidal state. Prasad and Hattiangadi<sup>7</sup> find by cataphoretic experiments that the gel forming mixtures contain colloidal particles which are negatively or positively charged according as the mixtures are alkaline or acidic. Billiter<sup>8</sup> has also similarly shown that the particles in a silicic acid sol are negatively charged in alkaline and feebly acidic solutions and positively at higher hydrogen ion concentrations of the mixtures. Lösenbeck<sup>9</sup> finds from the migration velocity experiments that the particles in a silicic acid sol are negatively charged and in the presence of the increasing amount of hydrochloric acid the charge decreases, reaches the iso-electric point and is then

reversed until the positive charge is much greater than the negative one.

The next process in the gelation is the coagulation of the silicic acid sol by electrolytes present in the mixture. Prasad and Hattiangadi<sup>10</sup> have shown that the process of gelation is influenced by the presence of electrolytes and non-electrolytes in the same way as the coagulation of the dialysed sols of silicic acid. Also Smoluchowski's equation for the coagulation of a colloidal solution by electrolytes<sup>11</sup> applies fairly well within certain limits to the gelation of silicic acid (*cf.* Prasad, Mehta and Desai<sup>12</sup>).

As the coagulation of the silicic acid sol progresses the charge on the colloidal particles decreases, due to which (*cf.* conclusions of Dhar and Collaborators<sup>13</sup>) and owing to the amphoteric nature of the silicic acid the degree of hydration of the silicic acid particles increases and causes an increase in the viscosity of the gel-forming mixtures. Prasad, Mehta and Desai<sup>14</sup> find that during gelation the particles of silicic acid increase in size and the ultimate particles in the gel are bigger than those present in the sol. The increase in the size of the particles also, therefore, contributes to the increase in the viscosity of the gel-forming mixtures.

The viscosity of the mixtures increases very slowly in the beginning of gelation, the increase in the acidic mixtures being slower than in the alkaline ones, and then very rapidly until it reaches a constant value. Hurd and Letteron<sup>10</sup> also find that during gelation the surface tension of the mixtures changes slowly in the beginning, progresses uniformly for sometime and then reaches a limiting value. The behaviour of alcohols towards the alkaline and acidic mixtures, however shows that the increase in viscosity depends upon the rate of gelation of the mixtures (*cf.* Prasad, Mehta and Desai<sup>12</sup>). The time-viscosity-curves are continuous which indicates that the formation of crystalloidal silicic acid, its going over to the colloidal state, the coagulation and agglomeration of the colloidal particles, their change in hydration and the linking of the hydrated particles form a continuous process and do not take place in any definite steps (*cf.* Prasad, Mehta and Desai)<sup>15</sup>.

With an increase in the viscosity of the gel-forming mixtures their elasticity also increases. The whole mixture begins to acquire an appearance of a solid and the gel is said to have set. The time of setting of the gels has been measured by Fleming<sup>16</sup> by the criterion that the vessel containing the mixture can be inverted without the

gel flowing out. Fells and Firth<sup>17</sup> find that the setting time is given by the maximum pressure required to blow or suspend a bubble of air or of mercury or of chloroform coloured with iodine, through the mixture. Prasad and Hattiangadi<sup>18</sup> have measured the setting time by an optical method which has an advantage over other methods in that the setting process is not altered by any kind of disturbance. Hurd and Letteron<sup>19</sup> find that the setting time can be conveniently measured by inserting a short stirring rod at an angle of about  $20^\circ$  to the vertical into the mixture: the gel is taken as set if the rod remains standing in that position.

The setting time of the gels depends upon the concentration of the acid and the silica content of the mixture. Fells and Firth<sup>6</sup> find that it does not vary with temperature within  $0^\circ$  to  $45^\circ$  but Hurd and Letteron<sup>19</sup> have shown that the gelation is affected by temperature in much the same manner as are homogeneous chemical reactions. The neutral or slightly acidic mixtures ( $p_H$  near about 7) set in minimum time. The increase in setting time has been attributed by Holmes<sup>3</sup> and by Fells and Firth<sup>6</sup> who have observed another minimum time when concentrated acids are used, to the catalytic influence of the  $H^+$  and  $OH^-$  ions and the dehydrating influence of the non-ionised molecules of the acids. But Hattiangadi<sup>20</sup> has shown that the variation in the setting time is due to the variation in the nature and the density of charge on the colloidal particles of silicic acid.

The gels obtained from the coagulation of the positively and negatively charged sols are distinctly of two types; the alkaline mixtures give an opaque gel which appears bluish in reflected light and the acidic ones a translucent gel appearing pinkish white (*cf.* Prasad and Hattiangadi<sup>18</sup>). Kröger and Fischer<sup>21</sup> find that the plastic properties of the silicic acid gels also increase in passing from the acid to the alkaline gels.

On examining the process of gelation of silicic acid through an ultramicroscope Bachmann<sup>22</sup> finds that the amplitude of the movement of the ultramicroscopical particles diminishes and their size increases and at last the structure becomes ultra-microscopically homogeneous. According to van Nügli<sup>23</sup> the gelation is caused by the separation of numerous crystalline micelles each of which carries round itself concentric shells of the dispersion medium. The solidification is caused by the adsorption of the major part of the fluid on the micelles. According to Krishnamurti<sup>24</sup> the gel formation takes

place by the union of micelles, which are hydrated particles, enmeshing the intermicellary liquid. The water associated with the particles and the enmeshed water have, respectively, been called "fixed" and "free" water (*cf.* Fells and Firth<sup>25</sup>).

Fergusson and Applebey<sup>26</sup> have shown by the constancy of the composition of the syneretic liquid that it is the free water which is given out during the syneresis of the silicic acid gel. They consider syneresis as further coagulation of the original sol, for the factors which accelerate the setting process also increase the velocity of syneresis. Bonnell<sup>27</sup> finds that the volume of syneretic liquid is least with gels having  $p_H$  near about 8 and it increases as the temperature and the acidity or the alkalinity of the gel is increased. The shrinkage of the gel walls during syneresis also increases with an increase in the alkalinity of the gel (*cf.* Kröger and Fischer<sup>21</sup>).

The water contained in the gel can be removed by dehydrating it, say, by desiccating it over sulphuric acid (*cf.* van Bemmelen<sup>28</sup>). Desai<sup>29</sup> has shown that the rate of loss of water depends upon the  $H$ -ion concentration of the gels; it is least in neutral gels and increases with an increase in the acidity or alkalinity of the mixtures. During the process of dehydration some of the fixed water is changed into free water probably because of the tendency of the silicic acid particles to form crystalline anhydrous silica. Scherrer<sup>30</sup> has shown by X-ray method that the dry silicic acid gels possess a certain crystalline structure.

During the union of micelles capillaries are formed in gels. The needles of salts obtained by Fells and Firth<sup>6</sup> are formed by the concentration of the salt solution due to the loss of the solvent at the ends of the capillaries during the dehydration of the gels. The existence of the capillaries is also indicated by the fact that when a dried gel is placed in water it immediately crumbles into pieces because of the distension of the walls of the capillaries during the adsorption of water (*cf.* Bhatnagar, Prasad and Ohri<sup>31</sup>).

Holmes, Kaufmann and Nicholas<sup>32</sup> have found that on striking, the gel emits a musical note; the pitch of the note increases as the amount of the dispersion medium in the gel is decreased. By measuring the frequency of the note emitted by the gel and its elasticity it has been shown by the author<sup>33</sup> that it behaves as an isotropic substance.

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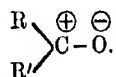
## On Keto-methylene Condensation.

By UMAPRASANNA BASU.

Although the condensations of carbonyl compounds with substances containing a so-called reactive methylene group, have been extensively investigated, it may be said that our conception of the mechanism of these reactions remains as yet indefinite. The consequence has been that a most important chapter in Organic Chemistry of a very great synthetic possibility, inspite of the massive collection of derivatives, lacks in its theoretical fundamentals.

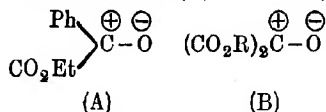
In the literature difference of opinion with regard to reactivity of the carbonyl group is largely in evidence, where the main issue has been whether the carbonyl group acts as an enol (*cf.* Haworth, *J. Chem. Soc.*, 1908, **93**, 1943 ; 1909, **95**, 480 ; Ingold, *ibid.*, 1921, **119**, 329) or as a ketone (*cf.* Kohler and Corson, *J. Amer. Chem. Soc.*, 1923, **45**, 1975 ; Corson, Hazen and Thomas, *ibid.*, 1923, **45**, 915 ; McRae and Kuchnarn, *ibid.*, 1930, **52**, 3377). Again it may be noticed that the reactivity of the carbonyl group itself cannot be regarded as the sole factor in keto-methylene condensation but is also influenced by the nature of the reactive methylene group. Thus benzophenone which does not react with ethyl cyanoacetate has been, however, found to condense with malononitrile by Schenk and Frinker (*Annalen*, 1928, **462**, 267).

If we now imagine that the double bond present in the carbonyl group of a ketone,  $R \cdot CO \cdot R$  reacts as if it contained one covalency and one electrovalency (so-called "mixed double bonds") (*cf.* Lowry, *J. Chem. Soc.*, 1923, **123**, 822). The ketone might then be represented as



Then in its reaction with a compound of the type  $H \cdot X$  ( $X$ =negative complex) the tendency of oxygen will be to attract the positive ion  $H^+$ . This tendency will be the greater the more

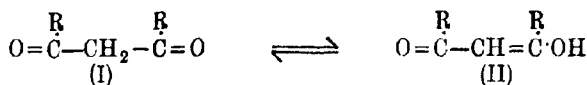
electropositive  $RR'$  are. The reason for the activity of benzoyl-formic ester (A) and oxomalonic ester (B) as found by Kohler, Corson



and others (*loc. cit.*) might thus be sought for in the factor indicated above. On this supposition, again, the stronger the negative group X, the more readily will the hydrogen leave it for the carbonyl group. Actually this has been found to be the case in the condensation of

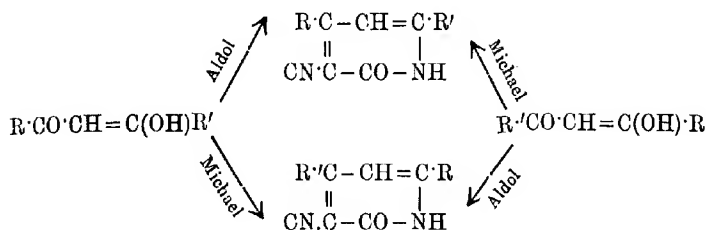
benzophenone  $(\text{Ph})_2\text{C}^{\oplus}\text{O}^{\ominus}$ , with malononitrile where the hydrogen atom of the methylene group is rendered extremely labile by its association with the two cyano groups (*cf.* Rice, "Mechanism of the Homogeneous Organic Reactions from the Physical Chemical standpoint," p. 52). These do not militate against the idea of Ingold who supposes that the relative ease with which a ketone reacts with a reactive methylene group is dependent on their capacity to pass into the enolic form, as this conception is independent of the idea that unenolised ketones can also react with active methylene groups under suitable circumstances. That is, to assume enolisation as the cause of a certain reaction is one thing, but to maintain on experimental grounds that wherever enolisation is possible, the relative ease of reaction is greater, is another.

Looking more critically, whilst in the case of simple ketones the enolised structure is only a matter of possible representation, the case of 1:3-dicarbonyl compounds is entirely different, as these latter actually contain an equilibrium mixture of the keto (I) and enol (II) modifications in the liquid or solution state.



The question is, which of the two forms is more reactive when both are simultaneously present? Here also there are two different views, one, in which it is assumed that the reaction of a dicarbonyl compound with a substance containing a methylene group takes place through the enolic form of the former, and the other, in which the reaction is supposed to occur through the ketonic form of the dicarbonyl compound. It is a difficult problem to distinguish between these two types of reaction, one, a Michael (ethylenic

addition) and the other an aldol, as both are fundamentally additive in character. The problem is still more complicated when the case of an unsymmetrical  $\beta$ -diketone is again considered. This diketone may exist in two different enolic modifications which would then give rise to two isomeric pyridone derivatives (in condensation with cyanoacetamide), whether the reaction takes place with the ethylenic linkage or the carbonyl group present in the molecule thus:



To have a precise idea regarding the mechanism of such a reaction, it is therefore essential to know whether one or both of these enolic isomers are present when the reaction with the methylene group takes place. But instead of several investigations both physical (Perkin, *J. Chem. Soc.*, 1892, **61**, 832; Smedley, *ibid.*, 1910, **97**, 1486; also cf. Sidgwick, *ibid.*, 1925, **127**, 907) and chemical (cf. Meyer, *Annalen*, 1911, **380**, 242; Ber., 1912, **45**, 2846; Scheiber and Herold, *Ber.*, 1913, **46**, 1695; *Annalen*, 1914, **405**, 295; Dieckmann, *Ber.*, 1922, **55**, 2470; Weygand, *Annalen*, 1927, **459**, 99; Ber., 1929, **62**, 574; Claisen, *Ber.*, 1926, **59**, 144) there is no real answer to the question as to what is the definite constitution of any particular enol? Now as the enolisation is found not to be exclusively limited to one particular carbonyl group and further considering Lowry's view (*J. Chem. Soc.*, 1923, **123**, 2114) that the two enols may be regarded as tautomeric, since, although they are usually written in two different ways, they are in fact not isomeric but identical, the problem becomes still more difficult.

However, it may be said now that in an 1:3-dicarbonyl compound the mechanism of ketone reactions with regard to compounds containing a reactive methylene group seems to be different from what the case is when a simple carbonyl compound is considered. To cite instances two great differences in the reactivity of simple carbonyl compounds and the dicarbonyl compounds have been noticed: (a) in the presence of hydrogen chloride a carbonyl group

condenses with a reactive methylene group (cf., Claisen, *Annalen*, 1883, 218, 172), whereas in the latter case no condensation with a reactive methylene group is brought about in the presence of the acid condensing agent (Basu, *J. Indian Chem. Soc.*, 1932, 7, 481); (b) according to Thorpe (*J. Chem. Soc.*, 1919, 115, 639) the presence of a tertiary carbon atom adjacent to the carbonyl group prevents the condensation with cyanoacetamide, whereas in an 1:3-dicarbonyl compound the presence of such tertiary carbon atom does not inhibit condensation with cyanoacetamide (Basu, *loc. cit.*). This reveals some sort of difference between a simple carbonyl compound and a dicarbonyl system. Consequently the point here is whether the explanation of Stewart and Baly (*J. Chem. Soc.*, 1906, 89, 489) that the reactivity of keto-enol compounds is due to the formation of a nascent carbonyl group during the tautomeric interchange of the system, is a general one and is also applicable in the case of dicarbonyl compounds. By destroying the possibility of nascent carbonyl formation, therefore, the reactivity of these dicarbonyl compounds with an active methylene group (e.g., 'CH<sub>2</sub>' in cyanoacetamide) would be considerably diminished. But experimental evidences, so far obtained (Basu, *J. Indian Chem. Soc.*, 1930, 7, 481, 815; 1931, 8, 119, 319) from the condensation reactions of cyanoacetamide with several O-ethers of the dicarbonyl compounds go directly against the above hypothesis. This would be more clear from the following table.

*The yield of the condensation product from an enol and its corresponding O-ether, and the substituent at the β-position of the unsaturated carbonyl compound.*

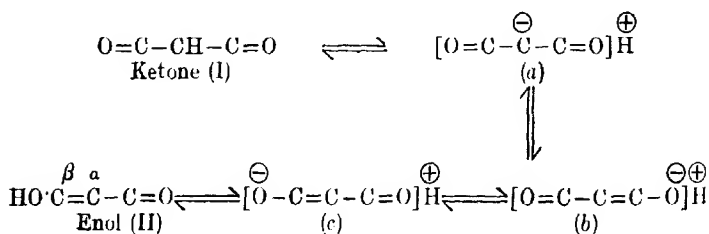
Enol. →	Yield. →	Substituent. ←	Yield. ←	Enol-ether.
Me HO·C=CH·CO·p-Tol	96%	Methyl	98%	Me EtO·C=CH·CO·p-Tol
Me HO·C=CH·CO·Ph	80	„	88	Me EtO·C=CH·CO·Ph
Ph HO·C=CH·CO·Me	20	Phenyl	30	Ph MeO·C=CH·CO·Me
Ph HO·C=CH·CO·Ph	65	„	70	Ph EtO·C=CH·CO·Ph
Ph HO·C=CH·CO·p-Tol	66	„	72	Ph MeO·C=CH·CO·p-Tol
Me HO·C=CH·CO·OEt	35	Methyl	35	Me EtO·C=CH·CO·OEt
p-Tol HO·C=CH·CO·Ph	34	Tolyl, anisyl	50	C <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> MeO·C=CH·CO·Ph

In each case the ethylenic bond present was found to be responsible for the condensation and it appears that there is a marked relationship between the behaviour of a dicarbonyl compound and its enol ether. The above table also shows that the enol ethers which do not contain any mobile hydrogen atom are also extremely reactive; so there is no apparent reason to believe that the reactivity of the dicarbonyl compounds is essentially connected with the dissociability of the mobile hydrogen atom or in other words with the nascent carbonyl group generated during each successive tautomeric interchange of the dicarbonyl compounds as Bardhan (*J. Chem. Soc.*, 1929, 2223) supposes. Further if the mobile hydrogen atom of hydroxymethylenecyclohexanone be replaced by an alkyl group such that C-alkyl derivative is formed, the necessary consequence would be the presence of pure aldehydic phase of the dicarbonyl compound. No condensation with cyanoacetamide was noticed (Sen and Mandal, *J. Indian Chem. Soc.*, 1928, 5, 617 ; cf. also Sen and Basu, *ibid.*, 1927, 4, 54), with such a C-alkyl derivative, although the acetate of hydroxymethylenecyclohexanone (a system in which again the conjugated double bonded phase is present) readily condenses with cyanoacetamide (Sen, *J. Chem. Soc.*, 1915, 107, 1352). These show, therefore, that for the reactivity of the dicarbonyl compounds in such a reaction, all that is material is the presence of a conjugated double bonded system and that the condensation takes place at the ethylenic linkage which is the same as at the enolised centre. Or, in other words, it is a sort of Michael reaction. This also finds support from the following considerations.

It is well known that in a system of the type  $-\text{CH}:\text{CH}\cdot\text{X}$ , that is, when an ethylenic linkage occurs in the  $\alpha$ -position with respect to a so-called negative group ( $\text{X}=\text{CO}\cdot\text{R}$ ,  $\text{CO}_2\text{Et}$ , etc.), its reactivity is considerably enhanced as shown by its behaviour even towards ketonic reagents such as potassium cyanide, hydroxylamine, phenylhydrazine and substances containing a reactive methylene group. A  $\beta$ -diketone when represented by the enolic formula (II) is a system of this type, and, as is known, it readily reacts with ozone, halogens (the ethylenic reagents) as well as with hydroxylamine, phenylhydrazine, etc. Hence it will not be unreasonable to expect a reactive methylene group to react with the ethylenic linkage present in the system. When, however, the ethylenic bond contains further a contiguous hydroxyl group as in (II), the presence of which enormously increases the additive capacity of the double linkage (Meyer, *Annalen*,

1913, 398, 66), a preferential addition at the ethylenic linkage becomes more probable.

The question now arises what is the function of the basic condensing agent used in such reactions? As the mobile hydrogen atom present in the dicarbonyl compound is in an activated condition (cf. Usherwood, *J. Soc. Chem. Ind.*, 1923, 42, 1246), i.e., in a state of incipient ionisation owing to the presence in the molecule of a negative group ( $\text{CO}\cdot\text{R}$ ) which exerts a pull on the electrons involved in binding the hydrogen atom, the effect of the base now would be to remove hydrogen ions by forming the complex  $\text{HN}\equiv$  or introduce ethoxyl ions and thus increase the concentration of organic negative ions. Under these circumstances then the tautomeric interchange will be much accelerated as according to Lapworth and Hann (*J. Chem. Soc.*, 1904, 85, 47) the change of internal structure occurs more readily in the ions than when intramolecular atomic or group migration is involved (cf. also Knorr, *Annalen*, 1896, 293, 98; Wislicenus, *Ahrens. Sammlung*, 1898, 2, 230). This is but the general view that ionisation precedes tautomeric change which can be interpreted as a removal of the mobile hydrogen as a proton followed by the movement of the change in the electromeric ion (Lapworth, *J. Chem. Soc.*, 1901, 79, 1265; Ingold, Shoppee and Thorpe, *ibid.*, 1926, 1477) thus:



The equilibrium of the system will then depend mostly on the relative stabilities of the above three anions (a), (b) and (c) and the co-valent linkages by which the common cation (hydrogen, sodium or the complex  $\text{NH}\equiv$ ) associates with each of them. Amongst the three points, one carbon in (a) and the other two oxygen in (b) and (c) at which the cation can form the link, the latter two links having more powerful attraction for the cation specially in case of sodium or the complex  $\text{NH}\equiv$  will naturally favour the formation of the enol (II) which is regarded as an  $\alpha\beta$ -unsaturated ketone. Consequently its reaction with a substance containing a reactive methylene group will

be governed by the general principles of the mechanism of Michael reaction as established by Copper, Ingold and Ingold (*J. Chem. Soc.*, 1926, 1868; also Ingold, *ibid.*, 1930, 184).

Accordingly dividing the investigations into the following heads:

(a) Influence of substituents (positive and negative) at the position of the dicarbonyl compound represented by the enolic structure (II); (b) same at the  $\alpha$ -position of the dicarbonyl compound; (c) influence of the substituents at the methylene group of the reactant; it has been always found (Basu, *loc. cit.*) that a lighter substituent such as methyl whether in the enol (II) or its O-ether  $RO\cdot C:C\cdot C:O$  generally enhances the ease of the reaction and the yield of the condensation product, whilst in cases where the substituent is phenyl the yield is much reduced (*vide* Table). This recognises the already established principle that in Michael reaction "a  $\beta$ -substituent considerably reduces the tendency towards condensation. The effect is a spatial one, the larger the group, the stronger is the inhibition" (*cf.* Ingold, Perren and Thorpe, *J. Chem. Soc.*, 1922, 121, 1770). The principle was further established by condensing cyanoacetamide with dicarbonyl compounds containing a negative substituent (*e.g.*,  $CO_2Et$ ) at the  $\beta$ -position in their respective enols. Again it has been found (Basu, *loc. cit.*) that in cases where the yield is low, the rate of reaction is independent of the concentration of the dicarbonyl compound but proportional to the concentration of the other reactant (cyanoacetamide). This is in accordance with the principle (*cf.* Ingold and Perren, *J. Chem. Soc.*, 1922, 121, 1416) that a Michael reaction is a reversible one.

The identity of the condensation reaction studied with the Michael reaction is very complete thus:

(a) The low temperature and basic condensing agents which favour the Michael reaction, also favour the existence of the dicarbonyl compounds in their enolic form.

(b) Again Perkin, Smedly, and Meyer (*loc. cit.*) have shown that when a methylene hydrogen atom of an 1:3-dicarbonyl compound is replaced by an alkyl group, the tendency to enolise is diminished (*cf.* also Kon and Narayan, *J. Chem. Soc.*, 1927, 1586). In the condensations of cyanoacetamide with methylacetylacetone, ethylbenzoylacetone, etc., similarly the yields are reduced to a certain extent.

(c) A third characteristic of a Michael reaction is the enhanced reactivity conferred by  $\alpha$ -substituting negative groups (in unsaturated



ketones) as compared with  $\alpha$ -alkyl substituent. In the case of dicarbonyl compounds the influence of  $\alpha$ -negative substitution could not be followed as the influence of the basic condensing agent helps a rupture (Claisen, *Annalen*, 1896, 291, 70) of the substituted dicarbonyl compound (tricarboxyl compound diacetoacetic ester or dibenzoylacetone) into a normal dicarbonyl compound.

Lastly regarding the influence of the substituents in the methylene group it has been observed that the reactivity of the methylene carbon atom in all such reactions depends on the total negative nature of both the substituents and that if this does not reach a certain limit, necessary for facilitating the antecedent ionisation of the reactant  $R\cdot CH_2\cdot R'$  into its hydron and the negative organic

ion  $R\cdot \overset{\ominus}{CH}\cdot R'$ , the reactivity of the methylene group vanishes at least with respect to  $\beta$ -diketones. Thus the reactivity of the carbonyl group itself cannot be regarded as the sole factor in this condensation but an emphasis is also to be laid on the reactivity of the reactants, and consequently the inactivity of  $\alpha$ -cyanopropionamide,  $CH_3\cdot CH(CN)\cdot CO\cdot NH_2$ , with respect to acetylacetone as observed by Bardhan (*loc. cit.*) must also be sought for in the diminished negative nature of the methine group in the molecule undoubtedly owing to the presence of an extra methyl group. But still reference must be made to the work of Errera (*Ber.*, 1901, 34, 3691) who brought about a condensation of  $\alpha$ -cyanopropionamide with ethoxymethylene acetoacetic ester [ $EtO\cdot CH\cdot C(CO_2Et)CO\cdot Me$ ] at an experimental condition quite different from what has been done in the above investigations. Repeating experiments on similar lines, i.e., heating the reactants ( $\alpha$ -cyanopropionamide and acetylacetone) in presence of sodium ethoxide in a sealed tube, practically the whole of the dicarbonyl compound was hydrolysed and an extremely small quantity of a nitrogenous product (m.p.  $284^\circ$ ), on crystallisation from acetic acid, was obtained which however did not give any coloration with alcoholic ferric chloride.

Thus the investigations referred to, seem to establish mainly the following points:

(a) A fundamental distinction has been pointed out between a simple carbonyl group and that in conjugation, and the risk of carrying the analogy from one set of reactions to the other has also been shown.

(b) The enhanced reactivity of the 1:3-dicarbonyl compounds with respect to reactive methylene groups is due to the presence of an ethylenic linkage in conjugation with a carbonyl group. The idea of the production of a nascent carbonyl group in the dicarbonyl compound as being responsible for such reaction is therefore unnecessary.

(c) Whilst in the past the reactivity of the carbonyl compound was regarded as the sole factor in keto-methylene condensation, emphasis has been laid on the reactivity of the reactants other than the ketones. From this the idea of a certain limiting positivity of the reactants or the negativity of the carbonyl has been introduced.



## The Chemotherapy of Organo-metalloid Compounds.

BY SUDHIR CHANDRA NIYOGY.

The employment of organic compounds of arsenic and antimony for the treatment of trypanosomiasis, has now reached a stage when it is necessary to consider the mechanism of their activity. But it would be as well if it is admitted at the very outset, that the use of the organo-metalloid preparations as therapeutic agents, is only a passing phase in chemotherapy and that their function will ultimately be fulfilled by compounds of a more active but less toxic type, which will, moreover, contain no element, foreign to the human body.

The question whether the action of organo-metalloid compounds is direct or indirect, has not yet been satisfactorily settled. The pioneer worker in this field, Ehrlich, in his well known "receptor" theory, assumed that the parasites contained some particular groups which were capable of combining chemically with certain groups in the drug, forming in this way a complex, which interfered with the life process of the bacteria and thus brought about their destruction. In the case of arsenic and antimony compounds for the treatment of trypanosomal infection, it is assumed that the active group in the drug is the arsenic or antimony complex, and that the organisms themselves contain the "receptor" grouping. But very serious objection may be raised against such a theory. If the process of bactrecidal action is due merely to a combination of an active group in the parasite with the arsenical or antimonial complex of the drug, it is difficult to explain why insignificant changes in other parts of the molecule should so vitally affect the activity of the compounds. For example, it has been found that the ammonium salt of 4-carbamidophenylstibinic acid (Brahmachari's Ureastibamine) is an extremely active agent for the treatment of Indian *Kala-azar*, but the corresponding sodium or potassium salt is almost without any action. Again, when we consider the therapeutic action of compounds of the type Bayer-205 (which do not contain antimony or arsenic) it is clear that neither antimony nor arsenic is essential

for the destruction of trypanosomes; moreover, the removal of a sulphonic or methyl group from a particular position to the next one, gives rise to a product which is without any physiological action.

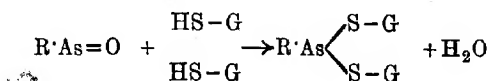
Being frequently confronted with difficulties of this nature, an attempt was next made to explain the action of organo-metalloid compounds, by assuming that they stimulate the production of certain antibodies, which bring about the destruction of the parasites. It was also assumed that owing to some pathological lesions, the system was unable to supply the necessary antibodies and the arsenical or antimonial employed, simply stimulated the natural function of the body. This indirect theory of anti-parasitic action has now been accepted with reluctance, because it has been found that chemical sterilization of experimental animals is possible, at least in some cases. The prophylactic use of Bayer-205 in Africa, has shown that when the healthy population in an infected area receives about 1g. of Bayer-205, in two doses, the number of new infections diminishes.

One cannot however, lose sight of the influence which certain positions in the benzene ring exert, in regard to therapeutic activity, at least in the case of aromatic antimony compounds. For example, in the case of aminophenylstibinic acids, it has been found that the *para* derivative is the least toxic as well as the most active of the three isomers and in fact, the other two isomers have scarcely any action. When however, the *ortho* position to the amino group is occupied by a negative group like halogen, the activity of the compound diminishes perceptibly, whilst with the substituent in the *meta* position, activity entirely disappears. One could conclude from this, that these two positions, *ortho* and *meta* with reference to the amino group when occupied, will lead to a reduced activity of the parent compound for the following reason:

Assuming the formation of a chemical complex between the active group or groups of a drug and the parasite, the molecular dimensions of which are undoubtedly large, one could imagine that steric considerations might come to play, if the positions adjacent to the active group be occupied. In the particular case referred to above, one must first of all ascertain, whether it is the amino group or the stibinic acid group, that enters into combination with the parasite. If it is the latter, the position next to it must be free for an easy com-

bination, whilst the *meta* position with regard to this group, if occupied, is not likely to exert very great steric influence. In the case of 4-aminophenylstibinic acid, a substituent in *meta* position to the stibinic acid complex does not naturally affect the physiological action but a substituent in *ortho* position to this group, gives rise to an inactive product. Probably, in this particular instance, it is the stibinic acid radicle and not so much as the amino group, that enters into combination with the parasite.

It is apparent from what had been stated above that the true mode of action of organo-metalloid compounds is still a matter of speculation but the recent work of Voegtalin (*Physiol. Rev.*, 1925, 5, 63) on the chemotherapy of arsenicals is of great importance, in that, it throws a flood of light on the obscure problem. Voegtalin assumes that the arsenic compounds are reduced in the body to corresponding arsine oxides, which in turn, combine with the reduced glutathione of the tissues.



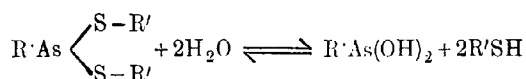
It has also been demonstrated by Voegtalin (*loc. cit.*) that trypanosomes contain SH groups (by nitroprusside reaction) similar to those present in glutathione and his hypothesis for trypanocidal activity appears to be based on the combination of the arsine oxide with SH group of the bacteria, forming in this way a complex which leads to the destruction of the parasites. In support of the assumption (that the arsine oxide does combine with SH groups, if present), he has established the following:

1. Simultaneous injection of sodium thioglycollate and the minimum fatal dose of 4-oxyphenylarsine produced a delay in the death of the animal.
2. Feeding with glutaminic acid and cystine affords protection against a fatal dose of 4-oxyphenylarsine oxide, administered 3 hours later.
3. Injections of compounds containing SH group, simultaneously with a trypanocidal drug, lowers the rate of disappearance of trypanosomes, from an infected animal.

The conclusions that might be legitimately drawn from these observations, seem to indicate, that the decrease in the activity of an active trypanocide, when injected simultaneously with compounds

containing a large number of SH groups, is due to greater part of the drug being removed from active service, but no deduction, concerning the nature of trypanocidal activity, is logically justified.

In a recent paper Gough and King (*J. Chem. Soc.*, 1930, 672) have put forward an ingenious hypothesis to explain the trypanocidal action observed with compounds of the type benzamide-*p*-thioarsenite, prepared by the condensation of benzamide-*p*-arsenic acid and  $\alpha$ -thiolacetic acid. The amide ester has been found to be superior, both in toxicity and therapeutic activity, to the free arsenic acid. To explain the activity of the compounds of this class, the authors have put forward the following explanation. It has been found that these complex arsenic acids are slowly hydrolysed, even in neutral solution, with the regeneration of small amounts of trivalent arsenious acids,



which have been found to be much more toxic than the pentavalent arsenic compounds, and the continuous production of minute quantities of this highly toxic trivalent arsenious acid in the tissues, maintained over an extended period, is responsible for the complete disappearance of trypanosomes, with resultant cure.

Gough and King came to experiment with the amides, after they had noticed that the presence of carboxyl or sulpho group, lowered the activity of an arsenic acid derivative. This however, is open to serious objection. Quinoline- $\alpha$ -carboxylic acid and acridinic acid are inactive no doubt, but 2-phenylquinoline-4-carboxylic acid has pronounced antipyretic properties, which are much superior to that of 2-phenylquinoline itself. Thus it cannot be assumed that the inactivity of 4-carboxyphenylarsenic acid and other allied compounds is simply due to the presence of carboxyl group. A further assumption which Gough and King have made to explain the lack of activity of compounds containing free carboxyl or sulpho group in addition to arsenic, is that these compounds are excreted rapidly, even when the pentavalent arsenic acid is reduced to trivalent arsenious acid, on account of the presence of "solubilising" groups". By destroying the salt forming nature of the carboxyl group through the formation of amide, one however, does not easily get over this difficulty. The example of 2-phenylquinoline-4-carboxylic acid

mentioned above, furnishes really an instance which contradicts the solubilising hypothesis of the authors. Further, the above authors seem to have overlooked the fact that the amide group will perhaps be the first to be hydrolysed, regenerating the carboxyl or sulphonic acids, of little therapeutic value. Assuming for the present, that the conversion of free carboxyl group into its amide (by depressing its tendency towards the formation of soluble salts) will improve the activity of organo-metalloid compounds, it is curious that the isomeric benzylbenzoate-stibinic acids which have been prepared (Niyogy, *J. Indian Chem. Soc.*, 1930, 7, 577) are without any action on the parasites of Indian *Kala-azar*. Moreover, it has been found that benzylbenzoate-2-acylamino-phenyl-5-stibinic acid (Niyogy, *J. Indian Chem. Soc.*, 1931, 8, 59) where an acylamino group is present in *para* position to the stibinic acid residue (as in 4-aminophenylstibinic acid) is quite inactive. This seems to indicate that the conversion of carboxyl group into its amide, is not the predominant cause for the improvement of therapeutic activity, but this change brings about some fundamental difference in the nature of the compounds.

In attempting to explain the lack of activity of the isomeric benzylbenzoate-phenylstibinic acids as also benzylbenzoate-2-acylamino-5-stibinic acid as compared to benzamide-4-arsinic acids (Gough and King, *loc. cit.*) many possibilities present themselves, but of these two seem to be of predominant importance. According to Voegtalin (*loc. cit.*) the trypanocidal action seems to depend on the reduction of pentavalent arsenic or stibinic acids to the corresponding trivalent oxides; the inactivity of the stibinic acids might be due to the inability of the tissues to reduce them to the corresponding oxides. In other words, these stibinic acids lie outside the reduction potential of the tissues. In fact it may be safely concluded, that the variation in the chemotherapeutic index of the derivatives of phenylstibinic acids, is in fact due to the variation of the necessary reduction potential, produced by the various substituents in *ortho*, *meta* or *para* position to the stibinic acid residue.

A further reason for the inactivity of the stibinic acids mentioned before, might be that they are removed from the system, arising in part to the great solubility of the corresponding sodium salts and in part, due to that lack of substantive properties for the tissues. This substantive effect of efficient medicaments, which keeps them in the body for long periods and allows them to exert a persistent and continuous action, has been clearly demonstrated in



the case of Bayer-205, and it undoubtedly plays an active part, in the action of antimonials. Thus the superior activity of trivalent arseno compounds over pentavalent arsinic acids, of silver salvarsan over salvarsan, of zinc sulpharsenol over sulpharsenol, in experimental trypanosomiasis, is undoubtedly associated with much longer persistence in the body.

If we admit however that the reduction potential of stibinic acids under consideration, is such that the pentavalent stibinic acid is capable of being reduced to the trivalent stibonous oxide (which is the first stage of the reduction usually observed) then in order to explain the inactivity of compounds like benzylbenzoate-phenylstibinic acid, one is forced to conclude that the so-formed oxide is not capable of combining with the thiol complexes of the tissues and then regenerate free stibonous acid through hydrolysis, which is likely to be the active agent. How far these groups affect the combination with the thiol group is not known and until we know this, the hypothesis put forward by Gough and King, must be taken up with caution.

In this attempt to explain the causes of activity of organo-antimonials and arsenicals, one great factor seems to have been lost sight of by most workers in the field. This relates to the colloidal nature of the active substances themselves and that of the system, in which the reaction is taking place. How far the electrical charges in such colloidal systems and how far the neutralisation of such charges leading to coagulation, are responsible for therapeutic activity, should be regarded as a fruitful field of research. Again, there is further room for speculation whether the difference in the reactivity of one and another compound, may not be due to the difference in the energies, for whilst the conventional chemical or structural formulae, may reveal nothing concerning the reasons of their specific action, the energy relations of the atoms or atomic groups, which make up the molecule, are the agents responsible for the development of specific activity. Should this assumption prove to be true, an interesting speculation naturally comes in—that accurate and scientific progress in chemotherapy will take place through the reduction of organic chemistry to series of mathematical conceptions in intramolecular physics.

## The Degrees of Freedom and the Constant $M/m$ .

By V. V. NARLIKER.

In Eddington's (Eddington: *Proc. Roy. Soc.*, 1931, **A**, **134**, 524) theory of the mass of the proton, the ratio of the masses of the proton and the electron comes as the ratio of the two roots of a quadratic equation and not as a result of the interaction between an electron and a proton as he earlier expected. It seems that this expectation is rather fulfilled in his theory but in a rather obscure way.

In the theory, three kinds of degrees of freedom occur: (i) the 136 degrees of freedom associated with two charges; (ii) the ten degrees of freedom associated with the neutron, and (iii) the metrical degree of freedom.

The suggestion presented here is that the ten degrees of freedom which are associated with the non-electrical aspect of the electron should be considered as inertial degrees of freedom just as the 136 are the electrical degrees of freedom; in other words, the ten degrees of freedom define the quality of mass-interaction. In this manner, the 10, 136, and 1 degrees of freedom are associated with two point-charge masses, placed in a world in which the presence of the other particles is also accounted for; so that these numbers for degrees of freedom are not pure abstractions. We will now proceed to explain what we mean by the ten inertial degrees of freedom.

It is clear at once that the degree of freedom being a fundamental concept of the theory, could not possibly be explained except in terms of something more fundamental, which does not come into the theory. But explanations can be given why we choose the number 10; we can show in fact that the Machian (Mach, "Mechanics") concept of mass, or even the relativistic concept, can be explained in terms of ten familiar degrees of freedom. When we have done this it may be permissible to say that the number 1847 ( $M/m$ ), although it apparently comes from the equation of a proton or electron, is really due to the ten degrees of freedom in the inertial interaction between an electron and proton.

Thirty years ago, Mach propounded that the concept of inertia is an interaction concept. An isolated body in the whole universe can

have no inertia; for the latter, in this case, becomes an idle concept. Two bodies are required to define the concept or quality of mass, and the 'quantity' of mass associated with a body would be influenced by the other bodies in the world. Einstein (*Contribution to the Maxwell Centenary Celebration*, 1931) specially showed that this part of Mach's philosophy was incorporated in his theory of relativity, although he seems not yet to be satisfied as to the manner in which the mass-points are introduced into the theory.

Mach's definition of mass is this: the ratio of the masses of two bodies may be measured by the negative reciprocal of the respective accelerations induced in the two. We enquire: What are the degrees of freedom associated with two mass-points of the Newtonian world that would disturb the ratio? If the fundamental mass-points, (electron and proton) are not symmetrical structures, three degrees each come from the orientation of each; we take these orientations into consideration because we assume there are other bodies present in the world: thus there are six degrees of freedom. In addition there are three due to the rotation of one about the other: these must be taken into account because the particles are not supposed to be symmetrical structures. The tenth is due to the distance between the masses which can be altered.

In the theory of relativity the corresponding ten degrees of freedom associated with the definition of mass are unfortunately obscured. The field of two non-symmetrical mass-points is given in terms of ten potentials but so also is any general field. But that should not prevent us from seeing in what way ten degrees of freedom are also associated with the relativistic mass.

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## **Mineral Metabolism of Farm Animals.**

BY KSHITISH CHANDRA SEN.

### *Introduction.*

For quite a long time research in nutritional problems meant the study of the body requirements of proteins, fats and carbohydrates. About half a century ago the Munich School of Physiologists headed by Voit drew attention to the fact that minerals were necessary for the proper utilisation of foods. Thus Förster<sup>1</sup> showed that in the case of dogs which were given food from which the major part of the mineral matter has been extracted with hot water, the animals were unable to digest the food which was vomited unchanged after several hours. This aspect of the nutritional problem did not however attract much attention till the work of Hart, Steenbock, McCollum and others was started in 1906<sup>2</sup> in which the importance of providing sufficient mineral matter for the proper nutrition, growth and power of reproduction of farm animals was demonstrated. With the growth of our knowledge in vitamin physiology in recent times, the question of mineral requirements has assumed a place of great importance as in some cases it has been definitely shown that there is a marked correlation between the need of a vitamin factor and the assimilation and retention of certain mineral constituents.

The object of the present paper is to give a short summary of the present position of the problem of mineral metabolism with special reference to the nutrition of farm animals. It is not intended to discuss the vitamin question in detail. The importance of the problem from the point of view of Indian conditions will be touched upon as far as possible, though very few experimental results of this nature are available.

### *The Need for Minerals.*

It is important to determine, before we proceed further, the rôle of the minerals in the living organism. The animal body has been

analysed and the results are scattered throughout the literature. In general the following are the elements besides carbon, hydrogen, oxygen and nitrogen which are found in large quantity: calcium, phosphorus, sodium, chlorine, magnesium, potassium, sulphur and iron. It was at first thought that these were the only minerals essential for the body. It is however now known that there are other minerals, often present in traces, such as copper, manganese, iodine, etc., which are also necessary and serve important physiological functions in the growth and maintenance of the body.

We can classify the known functions of the minerals in the following way:

- (1) the maintenance of a proper osmotic pressure in the body fluids,
- (2) the maintenance of the neutrality of the blood and the lymph,
- (3) the maintenance of the proper physiological balance between various mineral ingredients in the blood,
- (4) to aid the processes of digestion and absorption, and
- (5) for the supply of various constituents of growing tissues and of internal secretions.

It is not necessary to say anything more now with regard to the above classification, as the importance of minerals for the above mentioned purposes is well known.

#### *Mineral Requirements.*

The question of mineral requirement is not a simple one and the amount varies in the case of different animals, with age and time. Thus a lactating animal requires a higher percentage of lime than a non-lactating one. Our information with regard to most elements is scanty; only definite results are known in the cases of lime and phosphoric acid. Mineral requirements as a rule are greater for a young animal than for an aged one, because in addition to the maintenance of the body, more minerals are necessary for the growing skeleton and tissues.

It has been known for a long time that milk is an ideal diet for the young and an interesting relation has been discovered between the rate of growth of an animal and the composition of its mother's milk.<sup>3</sup> In Table I the numerical relations are shown.

TABLE I.

Species.	No. of days in which wt. of the newborn is doubled.	Milk of the species contains % Protein.	Ash.	CaO.	P <sub>2</sub> O <sub>5</sub> .
Man	180	1.6	0.25	0.049	0.056
Horse	60	2.0	0.38	0.114	0.131
Cow	47	3.5	0.72	0.161	0.189
Goat	22	4.3	0.81	0.191	0.219
Sheep	15	6.5	0.89	0.277	0.269
Pig	14	6.7	1.03	0.395	0.357
Dog	9	7.1	1.01	0.333	0.364

It will be observed that there is a remarkable correlation between the rate of growth of an animal and the mineral and protein content of its mother's milk. Since the minerals do not supply energy in any form, their function is entirely different from that of carbohydrate, fat or proteins. From the above table it is clear that the milk of a rapidly growing species contains a larger proportion of ash. This is of course intelligible from the fact that more mineral matter is necessary in these cases to build up the bone and the skeleton. A similar correlation is observed between the chemical composition of the body and that of milk of the same species as has been shown by Bunge. <sup>4</sup>

*The Evaluation of the Mineral Requirement.*

It has been stated already that only in the case of lime and phosphoric acid is the amount of mineral requirement known. An idea of the requirement for these two substances may be obtained from the following considerations. It is known that each of these ingredients is present in the animal body to the extent of about 1% of the body weight of pig and about 2 % in the case of bullock. On this basis, for an increase of 100 lbs. in the body weight, the CaO and P<sub>2</sub>O<sub>5</sub> requirement will be about 1 lb each. Godden and his co-workers <sup>5</sup> have found in metabolic experiments with pigs that only 50 % of the intake of these minerals is retained under normal favourable conditions, and hence 2 lbs. of these minerals will be necessary for a 100 lb. increase of live weight. For a calf nearly double these amounts are necessary. Thus a calf putting on 1½ lbs. weight per day must therefore absorb from the intestine and retain approximately ½ oz. of

lime per day and a pig about  $\frac{1}{4}$  oz. Ten pounds of cow's milk contain roughly  $\frac{1}{4}$  oz. of lime and  $\frac{1}{8}$  oz. of phosphoric acid. A cow giving 30 lbs. of milk per day is therefore subjected to a drain of  $\frac{3}{4}$  oz. of the former and 1 oz. of the latter. The hen laying an egg a day, is perhaps the largest producer in proportion to body weight. An egg production of 200 per annum requires  $1\frac{1}{4}$  lbs. of lime.

It appears from the work of Sherman and Hawley <sup>6</sup> that with ordinary rations about three times the amount required for constructional purposes should be provided. That means, in the case of a young calf, that the ration should contain about  $1\frac{1}{2}$  oz. of lime per day and in the case of a young pig about  $\frac{3}{4}$  oz. A milch cow giving 30 lbs. per day should have about 2.5 oz. For animals grazing on good pasture these amounts are available. Good pasture contains about 1% of lime in dry matter, so that a cow consuming grass equivalent to 20 lbs. of hay would obtain just over 2.5 oz. On poor pasture however the percentage of lime may be as low as 0.5, and on such grazing she would receive only half of the amount of calcium needed for a 30 lbs. milk yield. On indoor rations, the likelihood of deficiency would be even greater, as most concentrates are relatively poor in calcium. Thus for example it would take 2 cwt. of a mixture of oats, bran and maize to yield 3 oz. of lime. The danger of calcium deficiency arises therefore either when grazing on poor pasture or during indoor feeding on concentrates. <sup>7</sup>

A good deal of attention has been paid to the requirements of lactating animals where the need for both these minerals is high. Large numbers of experiments have been reported by various investigators to keep an animal in positive calcium balance or to keep the animals in equilibrium. Forbes and his co-workers <sup>8</sup> were unable to obtain a positive calcium balance with cows during the first half of lactation, despite an abundant supply of calcium, phosphorus and other minerals. Hart and others <sup>9</sup> succeeded in obtaining a positive calcium balance by feeding alfalfa hay. In later experiments they could only reduce, but not make positive, the negative balances of milking cows by substituting alfalfa hay for timothy hay. These latter results were attributed by them to a faulty curing of the hay which destroyed the vitamin assisting calcium assimilation. Many other authors record beneficial effects from feeding fresh green food. Hart, Steenbock and Hoppert <sup>10</sup> found that with milking goats, the administration of cod liver oil converted a negative to positive calcium balance, but the oil was not well tolerated. In some experiments at

the Rowett Institute in the case of young hog pigs on a ration of maize, middlings, oat meal and blood meal, cod liver oil raised the calcium retention from a minus quantity to over 60% of the intake. Irradiation with artificially produced ultraviolet light produced a similar effect both in growing and in lactating animals. Thus, for example in the case of young pigs, exposure to light from a carbon arc lamp for one hour daily raised the calcium retention from 0.46 gram to 2.1 gram. In lactating goats the effect of light was to diminish the loss of calcium or to convert a loss to a gain.<sup>11</sup>

*Balance between Minerals.*

The question of mineral requirement is intimately connected with assimilation and retention, and balance between different mineral constituents. It is becoming evident now that the ingestion of one mineral may profoundly affect the retention of another mineral. Thus Henderson<sup>12</sup> has found with pigs that when the ratio of lime to phosphoric acid in a ration is 1:1, there is an adequate assimilation and retention of both elements, but when the ratio is only 1:2.5, the balances are very much lower and the animals fare better under ultraviolet treatment. It is of course well known that a high variation in  $\text{CaO} : \text{P}_2\text{O}_5$  ratio in the diet causes either a low calcium or low phosphorus type of rickets in rats which is indeed the basis of Sherman and Pappenheimer's<sup>13</sup> rachitogenic diet. Phosphorus may be present in abundance and may be absorbed from the intestine in sufficient amounts, but unless a sufficient amount of calcium be present it cannot be used for bone construction, and the greater part may be lost in the excreta. According to Ingle<sup>14</sup> an excess of phosphorus may deplete the body of previously stored calcium.

The nature of the diet, in certain other respects, also affects the assimilation of calcium. Thus, for instance, a higher proportion of calcium appears to be absorbed from fresh pasture than from most other food stuffs. In the case of hay the method of curing is of some importance, assimilation being more difficult from hay that has been left lying out for a long time than from hay secured from minimum exposure to the elements. In the case of children, Blauberg<sup>15</sup> found the assimilation of calcium from human milk, cow's milk and an artificial food was respectively 82, 61 and 33 per cent. Sherman and Hawley<sup>16</sup> found that calcium in vegetables could not be assimi-



lated as easily as the calcium in cow's milk. The ratios of other constituents of the ration to calcium are also of some importance. According to Ingle<sup>17</sup> excess of magnesium may limit absorption. There is an optimum ratio of fat to calcium. The ratio of acid to basic radicles has also an influence, assimilation being more rapid when there is an excess of acid radicles. The influence of a proper  $\text{CaO} : \text{P}_2\text{O}_5$  ratio has already been mentioned. With regard to the assimilation of other minerals, it is probable that the amount of calcium in the diet affects assimilation of iron. With an ample calcium intake, the body can satisfy its needs from a smaller amount of iron than is the case when the intake of calcium is limited.<sup>18</sup>

A certain amount of controversy has centred round Bunge's theory<sup>19</sup> for the necessity of a correct balance of Na: K in the diet. He showed that an excessive ingestion of potassium salt causes an elimination of sodium and chlorine. This is of importance in practical feeding of farm animals, because a depletion of sodium and chlorine would tend to react unfavourably on the animals. Lengthy experiments on heifers carried out by Hart and his collaborators<sup>20</sup> have however shown the incompleteness of Bunge's theory. They found in the case of different groups of animals, fed on rations of different cereals, but all having free access to salt, that the amount of sodium chloride consumed bore no relation to the potassium content of the ration, either when used alone or when supplemented by potassium salts. But an interesting question has been raised with regard to the effect of an abnormal ratio of Na: K on the retention of other elements such as calcium. Thus Seeman<sup>21</sup> first suggested and Zander<sup>22</sup> supported the idea that an excessive K: Na ratio may be the cause of rickets. Aron<sup>23</sup> also considered it probable that such a ratio interfered with the deposit of calcium and bone formation in cattle, while Zuntz<sup>24</sup> has recorded that fodder which cause rickets usually show an excessive proportion of K to Na. In recent years Richards, Godden and Husband<sup>25</sup> have investigated the effect, on the metabolism of the growing pig, of increasing the proportion of Na to K by addition of sodium salts to a cereal ration, and have found that the addition of sodium chloride or sodium citrate led to increased assimilation and retention of nitrogen, calcium and phosphorus. In a later paper<sup>26</sup> it was found that the addition of potassium citrate to the diet decreased the retention of the above constituents. With regard to lime retention, potassium citrate led to a decrease while

sodium citrate showed an increased retention and the authors conclude that a high Na: K ratio may have a considerable influence on the calcium assimilation.

*The Inter-relation between Organic and Inorganic  
Constituents of the Diet.*

The first point that arises in this connection is the rôle of organic constituents on the retention of minerals and secondly the rôle of minerals in the phenomenon of digestion and absorption of the energy producing substances. Thus Auchinache<sup>27</sup> in a recent series of elaborate experiments with sheep finds that there is some unidentified substance in green pasture which is superior to cod liver oil in assisting assimilation and retention of lime and phosphoric acid. Godden and others<sup>28</sup> find that with pigs on a ration badly balanced with respect to CaO and P<sub>2</sub>O<sub>5</sub>, the addition of oils like cod liver oil, linseed oil and olive oil caused a rise in the calcium and phosphorus balances.

The question of the rôle of minerals on the digestion and assimilation of the organic constituents of the food has not been thoroughly studied, but the results obtained by Förster<sup>29</sup> are significant. When minerals were previously extracted from the food, he found that on this diet dogs died sooner than in complete starvation. Signs of disturbance of the digestive organs appeared early. They were soon accompanied by increased excitability and weakness of the neuromuscular system. The central nervous system was also affected, as was shown by the occurrence of convulsions and periods of drowsiness. A remarkable feature of the experiments was the profound disturbance caused by relatively small losses of inorganic salts from the system. The total mineral matter of the body at the beginning of the feeding with the diet from which all salt had been extracted was estimated at 1500 grams. During the experimental stage, the body lost phosphoric acid and sodium chloride in greatest amounts compared with other minerals, but the actual amount of loss of these minerals was only 30 grams and 7 grams respectively before death occurred as a result of mineral starvation. A well nourished body could lose a far larger proportion of its total protein, fat or carbohydrate without showing any marked disturbance of its functions.<sup>30</sup>

Regarding the effect of minerals on intestinal absorption, recent experiments by the writer<sup>31</sup> on the rôle of blood calcium on

carbohydrate metabolism point to some interesting probabilities. Thus with rats it has been found that a deficiency of calcium in blood causes a large decrease of sugar absorption from the small intestine. The question may now be raised as to the possibility of minerals functioning as a limiting factor in the carbohydrate utilisation by larger animals. Magee and Reid <sup>32</sup> have recently found that the addition of 0.2% phosphate increased the absorption of sugar by 50% in rats. These studies open out interesting fields of research in the physiology of absorption.

*The Relative Importance of Vitamins in the Feeding of Stock.*

There has been a good deal of confusion regarding the necessity of supplying vitamins to farm animals. Many results have been ascribed to unknown food factors which could easily be explained on the basis of their mineral constituents.<sup>33</sup> Thus according to Orr <sup>34</sup> in feeding experiments with fowls, where yeast is used as a source of vitamin B, some of the beneficial results obtained by giving yeast, can also be observed by giving a solution of inorganic phosphate and glucose in an amount equivalent to that obtainable from yeast. It is known that fowls have a high requirement of phosphorus while yeast is also a good source of phosphorus. The beneficial results of cod liver oil have been attributed to its vitamin content. It appears that vitamin D may be necessary for stock feeding. Apart however from its vitamin D content, the value of the oil may be due to its iodine content. Compared with ordinary feeding stuffs, many of which contain very little iodine, cod liver oil is rich in this substance and the results obtained by Smith <sup>35</sup> on pigs and Marine and Kimball <sup>36</sup> have shown that the administration of minute quantities of iodine may be followed by marked beneficial effects. With regard to the necessity of other vitamins, Theiler and his co-workers <sup>37</sup> in their experiments on cattle, sheep, goats and horses on rations deficient in vitamins, did not observe any symptoms which could be ascribed to vitamin deficiency. In the case of sheep, the addition of vitamin B to the ration led to no improvement in their condition. The lack of dependance of growing cattle on their rations for vitamin B<sub>1</sub> <sup>38</sup> and B<sub>2</sub> has been recently explained by the finding <sup>39</sup> that these factors are synthesised by the bacteria in the rumen of the species. In their experiments on pigs which are rapidly growing animals and therefore are likely to suffer from vitamin deficiency, Orr and his collaborators <sup>40</sup> could not produce any sign of

malnutrition on a ration deficient in vitamin A or C. Similar results have been obtained by Golding and his co-workers <sup>41</sup> with vitamins A and D who could not produce rickets in pigs on vitamin deficient diet although growth was stimulated in pigs of low weights on supplying pure milk and other substances. It is thus obvious that the requirements of the pig for these vitamins must be so low that there is no danger of deficiency on any ordinary ration. Crowther <sup>42</sup> and White and Roberts <sup>43</sup> have confirmed this view by practical experiments. Poultry <sup>44</sup> and also a calf <sup>45</sup> do not seem to suffer from a deficiency of vitamin C, and with regard to other vitamins the addition of cod liver oil to an already balanced diet is said not to give any improvement in growth, egg-laying or hatchability of the eggs.<sup>46</sup> The evidence on this point, however, is somewhat conflicting. Thus Foster <sup>47</sup> states that in an experiment conducted with two groups of hens, to ascertain the relative dietetic values of linseed oil and cod liver oil, it was observed that the linseed oil group developed the habit of eating their own eggs and others did not. On changing over the diets, within a week the group now on linseed oil began to eat their eggs and the former egg-eaters (now on cod liver oil) dropped the habit. Foster thinks that there is some connection between this depraved appetite (pica) and avitaminosis. It is interesting to note that the existence of a similar depraved appetite is well known to poultry-keepers in India. Hart and others <sup>48</sup> consider that the effect of cod liver oil on an unbalanced ration is due to its vitamin content. Baby chicks grow very well when cod liver oil is administered, or ultraviolet light is given. Since eggs are rich in vitamin A, some source of this substance is needed in the ration. There is good evidence to indicate that a close relationship exists between the diet of cows and hens and the vitamin A content of milk and eggs. The highest concentrations of vitamin A in these foods occur during the season when an abundance of fresh green forage is available. The lack of green forage for the winter feeding of dairy cattle and laying fowls can to a large extent be overcome through the use of properly cured leafy forage, yellow seeds, such as yellow corn and yellow roots.

From the practical standpoint therefore, the question of vitamin addition is not of much importance in cattle feeding. As all grains, grain offal, pasture, roots, etc., are rich in vitamins, there is little danger of naturally grazing farm animals suffering from a deficiency of vitamins. The only possibility of vitamin deficiency is in the

case of indoor animals fed on rations composed mainly of artificial foods. It is remarkable that the vitamin requirement diminishes when the ration becomes better balanced with regard to the known constituents of food.<sup>49</sup> According to McCarrison<sup>50</sup> if a ration be properly balanced with regard to the known constituents of food, it is hardly possible for deficiency diseases, *i.e.*, those due to lack of vitamins, with the possible exception of scurvy, to occur outside a laboratory.

*Mineral Deficiency and Diseases due to Malnutrition  
in Farm Animals.*

The object of this section is to record a brief account of the numerous observations made on the malnutrition of animals on a mineral deficient ration and its effect on maintenance, growth and reproduction. The deficiency of lime and phosphorus, both natural and experimental, has been the most investigated, and many cases of Rickets, Osteoporosis or Osteomalacia, soft bone, bent leg, etc., are to be found in the literature. Deficiency of chlorine, iron, potassium, sodium, magnesium and iodine also occurs in many parts of the world. In the case of a deficiency of calcium, it has been proved that a slowing of the rate of growth, rickets and various digestive disturbances may be induced.<sup>51</sup> In a long series of experiments to which reference has already been made, Hart, McCollum and Steenbock (*loc. cit.*) studied growth and reproduction in cattle on a restricted diet of various grains. It was observed that the wheat fed animals (a diet deficient in calcium) suffered from malnutrition. Their offspring were not carried to full term and those that were not born dead usually died several days after birth. Meigs<sup>52</sup> and Hart, Steenbock and Humphrey<sup>53</sup> have found that loss of calcium (in milch cows with a negative calcium balance) has a serious effect on the condition of calves. They may be small and weakly, or may not live. Further, there may be difficulty in getting the cows to breed and abortion is liable to occur, but the same cows give birth to healthy, full time calves when the ration is improved by the addition of calcium salts.

A deficiency of calcium or phosphorus in the diet leads to decreased rate of growth in growing animals and decreased production in full grown animals. The feeding of deficient mineral has a remarkable effect on such cases. Thus Theiler and others<sup>54</sup> showed that the feeding of bone meal to stock grazing on phosphorus deficient pasture resulted in a rate of growth nearly three times greater

than that of control animals on the same pasture without bone meal. The milk yield in this case also increased by 40%. According to a Rowett Institute experiment, in the case of pigs on a Calcium deficient diet, the gain in weight in 124 days was 69.3 lbs. as compared with 132.8 lbs. on the same ration with the addition of calcium rich salt mixture. Elliot and others<sup>55</sup> fed young pigs on a ration of oat meal, bran, blood meal and potatoes with some swede turnip, "marmite" and cold liver oil being added to prevent vitamin deficiency. The ration was markedly deficient in calcium. The animals became unthrifty as shown by a staring coat, a tendency to emaciation, lethargy and a stilted gait. By the end of the third month bony deformities were evident. *Post-mortem* examination of the bones showed a reduced calcium and phosphorus content, excess of osteoid tissue, and a disorganisation of the zone of proliferation of cartilage. Control animals on the same ration with the addition of a calcium rich salt mixture grew at the normal rate and remained in perfect health. A very significant result has been obtained with breeding animals. Davidson<sup>56</sup> in Cambridge working with sows found that deficiency of calcium was the cause of weak litters, with high mortality after birth, becoming progressively worse with successive generations. Breeding was impossible in the fourth generation. It was noted that there was an absence of udder development at parturition and an obvious lack of milk during the suckling period. In a somewhat similar experiment with cattle at Wisconsin, Hart and others<sup>57</sup> found that on a ration of ground oats and oat straw, cows failed to breed or gave birth to dead calves. These workers calculated that for normal reproduction, there should be 0.45 part of calcium per 100 of the ration.

Much attention has not however been paid to other minerals. McGowan and Crichton<sup>58</sup> studied the subject of iron deficiency in the case of young pigs. They found that with a deficiency of iron, the young pigs gained in weight at fully the normal rate, but were fat and flabby. The skin was paler than normal and in some cases the hæmoglobin was as low as 25 per cent. of the normal. The death rate was high. As a result of experiments on animals Höslin<sup>59</sup> has also suggested that deficiency of iron may be the cause of primary anæmia in children. Waddel and others<sup>60</sup> recently showed the physiological function of traces of copper in hæmoglobin building and Elvehjem, Hart and co-workers<sup>61</sup> have shown the necessity of copper as a supplement to iron in hæmoglobin

formation in the pig. Orr <sup>62</sup> states that a diet containing too little salt produces in cows a staring coat, lustreless eyes and a condition of general malnutrition with a decrease in milk yield. The condition appears to be due to a lack of chlorine, and can be rapidly cured by giving either sodium chloride or potassium chloride. An excess of chlorine however might lead to pathological symptoms. Thus McCollum <sup>63</sup> regards an inflammatory condition of the eyes, resembling xerophthalmia which he calls "salt ophthalmia" as due to excess of chlorine in the food.

So far we have been considering malnutrition in cattle more or less under experimental conditions. The importance of this mineral deficiency lies however in the fact that some deficiency diseases, due to lack of minerals, are common in all parts of the world. Thus Marine <sup>64</sup> studied the curative effect of iodine on goitre by observations on sheep in Michigan. Severe losses occurred there through goitre with which were associated certain pathological conditions and heavy death rate in lambs. Ennis Smith <sup>65</sup> in Montana found a striking case of the effect of iodine in preventing the birth of hairless pigs. Helmer <sup>66</sup> in British Columbia and Torrance <sup>67</sup> in Canada recommended administration of potassium iodide to sows, ewes and cows as a prophylactic measure against goitrous conditions. Numerous other experiments on the beneficial effect of iodine on a iodine-low ration have demonstrated its value in the dieting of farm animals.

The most important of recent contributions to the study of mineral requirement has been made on phosphorus deficiency by a group of workers in South Africa, and a very recent paper by Theiler and Green <sup>68</sup> summarises the position of aphosphorosis in ruminants with a bibliography of 150 papers. It is therefore not necessary to discuss this subject any further, but mention may be made of one of their interesting conclusions, that aphosphorosis may be made evident by blood analysis long before any clinical symptom of phosphorus deficiency appears. In a paper on "Pica" which means depraved or perverted appetite in animals Foster (*loc. cit.*) has brought together many interesting natural cases. Thus while wool eating in sheep may sometimes be due to the presence of external parasites, Green <sup>69</sup> records a serious outbreak of the habit among penned sheep fed on maize endosperm and minimal ration of auto-claved hay, "a diet faulty both in mineral and in vitamin content." Hutyra and Marek <sup>70</sup> consider the fault to lie in the low salt content and the ill-balanced

mineral ratio of the fodder. The same observers quote tales of Alpine hunters and mountaineers whose perspiration-soaked clothes were greedily licked by salt-starved mountain sheep.

An interesting form of pica is the habit of eating earth at the so-called "salt licks." This is found specially in tropical regions and salt licks are known to occur in the Punjab, in the Madras Presidency and in Hyderabad State. Some salt licks in South Africa are composed mainly of lime and phosphorus, whilst others may be rock salt or a mixture of sodium carbonate and bicarbonate. Recent analysis at Nairobi of the Lumbwa cave earth, which is largely used as a salt lick has shown that in addition to 5 per cent.  $\text{Na}_2\text{O}$ , there are also present 5 per cent.  $\text{Fe}_2\text{O}_3$  and up to 5.25 per cent.  $\text{Ca}_3(\text{PO}_4)_2$  <sup>71</sup>. An analysis of Madras salt licks by Newcomb <sup>72</sup> showed that the substances contained large amounts of iron and some iodine. Roy (unpublished data) in this laboratory has recently analysed several samples of salt licks and edible earths and has found that some of them contain appreciable amounts of lime and iron while others mainly sodium chloride, traces of carbonate and sulphate.

#### *Conclusion.*

In concluding this paper a brief reference may be made to the work done in India on this subject. An important investigation in this direction is that of McCarrison <sup>73</sup> on the goitre problem and the distribution of iodine in certain regions of India. With regard to lime and phosphorus deficiency, Davis <sup>74</sup> states that the low milk yield of cows in Bihar is due to deficiency of phosphorus in the pastures and McCarrison <sup>75</sup> has stated that in Bihar and on the Malabar coast mortality among cattle is high, sterility is common and the milk yield of cows is low. McCarrison suspects the cause to be lack of phosphorus. Smith <sup>76</sup> suggested that in many parts of the country the local fodders were deficient in mineral matter and Warth <sup>77</sup> considers that the deficiency of phosphorus is perhaps the most important problem in India. He also cites the work of Meggitt who found deficiencies of lime in Assam and Harrison's soil survey in Madras Presidency showing regional deficiencies. It is of course well known that soil deficiencies are reflected in the crops. Matson <sup>78</sup> has observed the beneficial effects of potassium iodide in cases of delayed shedding of calf hair and Nayudu <sup>79</sup> considers that iodine fed to young calves improves their appearance. Aiyer and Kayasth <sup>80</sup> have



recently studied the chemical composition of some fodders of the Central Provinces and Berar and find that these are deficient in phosphorus and lime. The poor stunted growth of the cattle in Chhattisgarh, may, according to them, be due to phosphorus deficiency. \* According to our own work here, some of the Muktesar pastures are markedly deficient in phosphoric acid and lime. There is thus no question that pasture in many parts of this country is deficient in nutrient minerals, but no systematic work has however been done to determine if, by the addition of suitable salt mixtures, the nutritive value of our pastures can be improved. Some experiments in our Institute, now in progress, seem to indicate that the addition of bone meal to the ration of dairy cows increases the milk yield. Since improvement in the condition of cattle is linked with the agricultural prosperity of our country, research into the food values of pastures and allied problems of nutrition in relation to Animal Husbandry is of urgent necessity. Pioneer work on the digestibility of fodders, silage, etc., and food values of different substances for growth and milk production has been done by Warth and collaborators<sup>81</sup> and by Lander and others<sup>82</sup> and it is now necessary to investigate the need of supplying minerals to the mineral deficient natural pastures of India for the proper growth, fertility and productive capacity of her cattle.

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## On the Constitution of Molecular Compounds.

By PRIYADA RANJAN RÂY.

It is well known that the chemical compounds can be conveniently divided into two main classes :

- (1) Simple compounds or compounds of the first order.
- (2) Molecular compounds or compounds of the higher order.

The constitution of the former has more or less been satisfactorily accounted for on the basis of the electronic theory of valency. But there is much difference of opinion regarding the structure of the latter. The object of the present paper is to make a critical examination of these different views and to suggest a probable solution of the problem.

To start with, it is necessary to sum up the fundamental assumptions underlying the electronic theory of valency as developed by Kossel, Lewis, Langmuir, Sidgwick and others.<sup>1</sup> This theory, which has been so fruitful in explaining the constitution of the simple compounds, recognises two main types of valency. These are *polar* or *electrovalency*, and *non-polar* or *covalency*. The polar or electrovalent bonds give rise to the formation of salt-like compounds or electrolytes, and result from the transfer of electrons from the positive to the negative constituent of the molecule. The covalent bonds unite atoms to form non-ionisable molecules by the sharing of a pair of electrons between them. In the majority of cases, chemical combination leads to the completion of the outer electronic structure of the combining atoms, which then resembles that of the nearest inert gas. The covalency has again been sub-divided into *normal covalency* and *co-ordinate covalency* or *semi-polar linkage* by Sidgwick and Lowry,<sup>2</sup> according as the electrons of the shared pair are contributed by both or only one of the combining atoms. It has been further shown that there are possible variations between these two extreme types of valency, due to the deformation of the orbits of electrons taking part in the formation of valence bonds. This is evidently connected with the magnitude of electron affinity of the combining atoms. The deformation of electronic orbits or

the shifting of the bond-forming electron pair gives rise to the formation of dipole molecules. semi-polar linkage or co-ordinate covalency obviously belongs to this intermediate type. Evidences regarding such deformation have been obtained from the study of ionisation, reflexion spectra, dipole moment, lattice energy, volatility, solubility, and specially of molecular refraction by Fajans and his co-workers.<sup>3</sup>

This conception of covalency, as arising from the sharing of electrons, has recently been placed on a firm theoretical basis in terms of the modern wave-mechanical principles by London and Heitler<sup>4</sup>, who have made use of Pauli's Exclusion Principle and the discovery of electron spin. Each covalent bond thereby consists of a pair of electrons with opposite spin moment.

Molecular compounds or compounds of the higher order are, on the other hand, formed by the union of two or more simple compounds, whose constituent atoms already exhibit their maximum valency. A study of the physical and chemical properties of these compounds indicates that there is a wide range of variation in the strength of the binding between the constituent molecules. The two extreme cases are represented by the so-called double salts, and the complex compounds of cobalt, chromium, platinum, etc. In double salts like alums— $\text{K}_2\text{SO}_4 \cdot \text{M}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ , carnallite— $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ , Mohr's salt  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O}$  etc., the individual ions of the constituent molecules do not lose their identity in solutions. Barring their definite composition and characteristic crystal structure, there is nothing to distinguish them from a mechanical mixture of the different simple compounds of which they are composed. On the contrary, the complex compounds, formed by Co, Cr and Pt etc., are characterised by exceptional chemical and physical properties, differing entirely from those of their constituent ions, the individuality of the latter being completely masked by that of the complex. Between these two extreme cases, however, comes in a class of compounds, which may reasonably be regarded as a transitional series connecting the two, the transition between which never occurs *per saltum* but only by insensible gradations. As typical representatives of this transitional series may be mentioned a large number of metallic ammines, like  $\text{CuSO}_4 \cdot 5\text{NH}_3$ ,  $\text{CuSO}_4 \cdot 4\text{NH}_3$ ,  $\text{NiCl}_2 \cdot 4\text{NH}_3$ ,  $\text{NiCl}_2 \cdot 6\text{NH}_3$ ,  $\text{AgCl} \cdot \text{NH}_3$ , etc., as well as complexes of the type  $\text{Me}_2\text{BeF}_4$ ,  $\text{Na}_3\text{AlF}_6$ ,  $\text{K}_2\text{SnCl}_6$ ,  $\text{KAgI}_3$ ,  $\text{KCdI}_3$ , etc. These transitional molecular compounds are partially dis-

sociated into their components in solution, responding more or less to the usual analytical tests for the individual constituent ions. The formation of a complex group in their case can, however, be demonstrated by physical methods, involving measurements of colour change, absorption spectra, electrolytic dissociation, distribution ratio, migration number, etc.

Hence a study of the general chemical and physical properties of the molecular compounds indicates that they may be classified into two main groups, (1) simple molecular compounds, and (2) complex molecular compounds.

The latter again can be sub-divided into (a) partial or imperfect complexes, and (b) complete or perfect complexes.

The partial or imperfect complexes form, as it were, a transition between the simple molecular compounds and the perfect complexes. Resolution of several complex molecular compounds, both of the perfect and imperfect types, into their optical enantiomorphs indicates a directional nature of the binding inside the complex.

#### *Electronic Constitution of Molecular Compounds.*

Two different main views have already been advanced to account for the electronic constitution of molecular compounds. The one advocated by Kossel, Magnus and others,<sup>5</sup> assumes that it is only the electrostatic attraction of the oppositely charged ions, or between ions and dipoles, that holds the partners together in all varieties of molecular compounds. The other view, supported mainly by Lewis, Sidgwick and Lowry,<sup>6</sup> maintains that the molecular compounds of all types are formed by the so-called co-ordination binding between the central atom and the groups around the latter. Both the electrons of each bond-forming pair are contributed by an atom of the surrounding groups, which was already in possession of such a lone pair. A third view, due to Sugden,<sup>7</sup> may also be referred to here. This author represents all molecular compounds as involving the formation of one-electron or singlet linkages. As the conception of singlet linkage is rather exceptional in character, and can scarcely be applied to the simple compounds of the first order, there is little justification to depart from the usual method of representation of the valence bonds in the case of the compounds of higher order. Besides, it is extremely difficult to fit it with the modern representation of the chemical bond on the basis of opposite spin moment and Pauli's Exclusion Principle. The unusual stability of some of the



complex compounds, such as  $K_4FeCy_6$ ,  $K_3CoCy_6$ ,  $[Co(NH_3)_6]Cl_3$ , etc., does not also warrant such an assumption in their case.

From a consideration of what has been said above, the electronic constitution of the molecular compounds evidently differs in the two main classes into which they have been sub-divided. The properties of the simple molecular compounds definitely indicate that the components are here held together simply by electrostatic attraction. The number of saturated molecules in a simple molecular compound is sometimes too large to permit of any other assumption. Thus, compounds of hexamethylene tetramine<sup>8</sup> with several co-ordinatively saturated complex cyanides have been obtained, which crystallise with a much larger number of water molecules than what is contained in the original salts. It is very difficult to locate the position of any electron-sharing between the constituent molecules in these cases. The behaviour of the complex molecular compounds, on the other hand, agrees admirably well with the assumption that true co-ordination bonds with sharing of electrons are at the basis of their formation. This is strongly borne out by the study of Raman spectra of molecular compounds. Well-defined Raman lines have been obtained in the case of  $[Co(NH_3)_6]Cl_3$ ,  $[Co(NH_3)_5Cl]Cl_2$ ,  $[Cu(NH_3)_4]SO_4$ ,  $[Cu(NH_3)_4]Cl_2$ ,  $[Zn(NH_3)_6]SO_4$ , and  $[Cd(NH_3)_6]Cl_2$ , indicating duplet bonds between Co-N, Cu-N, Zn-N and Cd-N respectively whereas the simple molecular compounds, so far as they have been examined, fail to give any Raman lines. The K-absorption edge of the chlorine atom of several complex compounds, studied by Stelling,<sup>10</sup> strongly supports this view. Absorption bands of the hydrated simple salts (simple molecular compounds) of several elements of the transitional group have also been found to differ completely from those of their perfect and imperfect complexes; the latter two, however, resemble each other more or less closely in this respect.<sup>11</sup> The preparation of several optically active modifications of complex molecular compounds, as already stated, lends further support to this view.<sup>12</sup>

We have also seen that the complex molecular compounds can be further sub-divided into perfect and imperfect complexes, though the binding in both is of a true co-ordination type. The question now arises whether there is at all any qualitative difference in their electronic constitution, or it is only of a quantitative nature. That there is indeed a marked difference, is shown by the difference in the magnetic susceptibilities of the perfect and imperfect complexes.

This is, however, only applicable to compounds with a paramagnetic central atom. It has been observed that the magnetic susceptibility of imperfect complexes is more or less identical with that of the simple ions, as obtained in the hydrated or anhydrous salts of the elements, forming the central atoms of these complexes. On the other hand, the paramagnetic susceptibility of a simple ion undergoes a profound alteration in many cases, often changing into diamagnetic character, when the ion forms the centre of a perfect complex. The above two types of complex compounds were named "Associated" and "Penetration" complexes by the present writer in a previous paper.<sup>13</sup> The associated complexes, correspond to the partial or imperfect type, and the penetration complexes to the complete or perfect type, indicating a closer approach of co-ordinated units around the central atom in the latter.

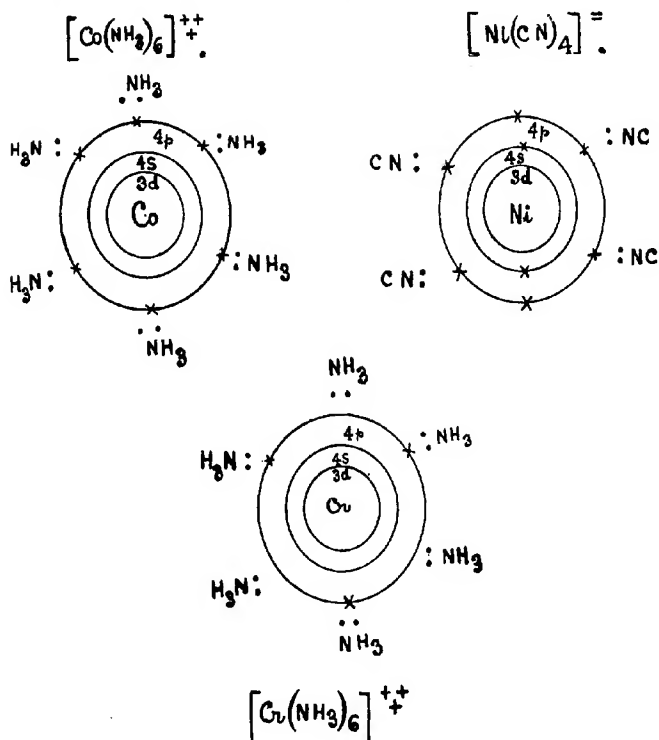
Bose<sup>14</sup> explains this difference in the magneto-chemical behaviour of the two types of complexes by assuming that in imperfect complexes, the binding is simply an electrostatic one as in the case of hydrates and double salts, whereas in the perfect complexes, electrons are shared in the inner incomplete shell of the central atom. From the considerations set forth above, there is not much justification, however, to assume that the units in associated complexes are held only by electrostatic attraction. Then again, several objections can be raised against Bose's view of electronic distribution in penetration complexes, which is based mainly upon Welo-Bose's rule,<sup>15</sup> previously suggested by them. This rule, as is well known, does not, however, hold good in many cases.<sup>16</sup>

Recently Pauling<sup>17</sup> has given an explanation of this difference in magnetic susceptibilities of perfect and imperfect complexes on the basis of wave-mechanical principles, in which he assumes that the electronic "eigenfunctions" of the central paramagnetic ion under the influence of strong chemical disturbance and perturbation due to the approach of other atoms, may, in certain cases, be re-distributed, giving rise to new "eigenfunctions," differing from the original ones in their form and binding capacity. This re-distribution often leads to an alteration in the magnetic moment of the central ion. But it is very difficult to explain the constitution and behaviour of the hexa co-ordinated nickel, cobaltous and copper complexes from this point of view. The penta co-ordinated copper compounds also present similar difficulties. There will not

be sufficient "d-eigenfunctions" left in these cases for the allocation of unshared electrons, nor will it be easy to account for the magnetic properties of these compounds. Assumption of the simultaneous existence of two different types of linkages—electrostatic and electronic—within the same complex, on the other hand, cannot be justified, specially in the case of compounds containing "chelate" groups like ethylenediamine, dipyridyl, dimethylglyoxime, etc. Reference may be made in this connection to the resolution of tris-dipyridyl nickelous chloride by Morgan and Bursfall.<sup>18</sup>

The valence bond in all the complex compounds should, therefore, be regarded to be of the co-ordinated covalent type, both the electrons of the shared pair in each bond being contributed by the co-ordinated unit or atom. The electrons in the incomplete shell of the central ion consequently take no part in the bond formation. And, as a matter of fact, we find that in the case of imperfect or associated complexes, the magnetic susceptibility of the central ion remains practically unaltered, except, in certain cases, neutralising the residual unbalanced orbital moments which contribute only a very small fraction to the total magnetic moment of the ions of the first transitional series, the spin moments of the electrons alone being mainly responsible here for the development of magnetic properties.<sup>19</sup> On the other hand, a profound alteration in the magnetic moment of a paramagnetic ion, when the latter acts as the centre of a penetration or perfect complex, definitely indicates a disturbance of the electrons in the incomplete d-shell of the ion. It is assumed that, in the case of strong co-ordination binding, sufficient energy is liberated to excite these mobile electrons, whereby they are raised to a higher level—the next p- and s-shells. That these electrons of the incomplete d-shell are very mobile and easily excitable, is evident from the fact that they often behave as valence electrons under suitable circumstances, in consequence of which the elements of the transitional series exhibit variable valencies. In all perfect complexes, formed by the elements of the first transitional series, with the exception of  $\text{Co}^{\text{II}}$  and Ni compounds, the electrons of the  $3d$ -shell of the central atom are excited by the energy of co-ordination to the  $4d$ -level, which can be filled up by six electrons. In the case of perfect  $\text{Co}^{\text{II}}$  and Ni-complexes, the electrons are raised to both  $4d_1$ - and  $4d_2$ -levels. Values, calculated on the basis of the above representation, agree remarkably well with experimental results. The only exceptions hitherto observed are  $\text{K}_4\text{CoCy}_6$  and  $\text{K}_2\text{NiCy}_3$ , which are diamag-

netic,<sup>20</sup> though according to the theory they should give magnetic moments of one Bohr-magneton each. This anomaly can, however, be accounted for on the supposition that these compounds are bimolecular, with a sort of metallic bond between the two molecules, so that the odd electrons of the latter mutually balance by the coupling of their spin moments. The eight or twelve shared electrons from the four or six co-ordinated units, as the case may be, are arranged symmetrically in the form of a more or less stable external shell around the central atomic core. It will serve no useful purpose to assign arbitrarily any definite quantum values to them. The following diagrammatic representation of the external electronic system in perfect complexes would make this idea clear.



- x electrons belonging to the central atom.  
 . electrons belonging to the co-ordinated atom.

The constitution of metallic carbonyls may also be similarly represented.

The view, suggested above, is developed from a consideration of the properties of complex compounds of the elements, forming the first transitional series; the data concerning the magnetic measurements for the simple and complex ions of the elements of other transitional series are not yet sufficiently large to permit of any useful discussion here.

In all the three types of molecular compounds discussed above, the source of attraction is the charge on the central ion: the units attracted are either ions or molecules with dipole moment. The firmness of binding increases gradually with the charge on the atoms concerned, and diminishes with the distance between them. The attraction exerted by the central ion leads to a deformation of the electronic orbits of the co-ordinated units. With progressive deformation the weak electrostatic bond in the case of simple molecular compounds is gradually transformed into a non-polar or rather semi-polar co-ordination bond in imperfect and perfect complexes. A quantitative distinction ultimately assumes a qualitative aspect. Thus the nature of the binding with all its varieties, as perceived in the compounds of the first order, finds its replica in those of the higher order. Or, to quote a biological analogy, there is a phylogenetic principle which governs the evolution in both the living and non-living matter.<sup>21</sup>

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## Temperature and Diamagnetism.

BY SHANTI SWARUPA BHATNAGAR.

The classical investigations of Curie (*Ann. chim. Phys.*, 1895, 7, v, 289-405) on the susceptibilities of a large number of substances over a wide range of temperatures have established the fact that the susceptibility of the diamagnetics varies little with temperature, while that of most paramagnetics decreases with increasing temperature. The next great contribution on the subject of temperature and diamagnetism is due to Honda and Owen (Honda, *Ann. Physik*, 1910, 32, 1027 ; Owen, *ibid.*, 1912, 37, 657) who systematically investigated the case of elements. As a result of these researches the diamagnetics can be classified into four types.

1. Those whose susceptibility increases with temperature, *e.g.*, boron, iodine and mercury.

2. Those whose susceptibility decreases with temperature, *e.g.*, copper and lead.

3. Those whose susceptibility is not influenced by temperature, *e.g.*, selenium, bromine, silicon, phosphorus and sulphur.

4. Those elements which show a marked change in the values of their susceptibility on melting, *e.g.*, bismuth.

This aspect of diamagnetism requires special investigation. The variation of susceptibility in the case of elements refers to the elemental state of matter and not to the atomic state. It is likely that in the building up of the element in mass, the electronic configurations may be of paramagnetic as well as of the diamagnetic types and that the temperature effects noted above may be due to the configurations which are paramagnetic in character. Interest in this work is further enhanced by the discovery of Krishnan that when single large crystals of naphthalene are melted the change in the diamagnetic susceptibility noted by Oxley (*Phil. Trans.*, 1914, 214, 109 ; 1915, 215, 79 ; 1920, 220, 247) disappears and the case of bismuth and the like elements referred to above under (4) therefore requires to be reinvestigated in light of this observation of Krishnan.

Precisely similar considerations make the investigation on the influence of temperature on diamagnetic compounds a rather attractive



problem and a series of researches have been conducted in the author's laboratories on this subject. As a result of these investigations we have found that in the domain of diamagnetic compounds also similar effects are noticeable as in the case of elements and they seem to be capable of satisfactory interpretation.

The most interesting case is that of water and some of the aliphatic alcohols which have been investigated in this laboratory by Messrs. R. N. Mathur and Abdul Azim. Here the diamagnetic susceptibility is found definitely to increase with temperature. Some of the results obtained are shown in Table I.

TABLE I.

Substance.	$-\chi \times 10^6$ .	% Change.	Range of temperature.
Water.	0.721-0.726	0.69	30°-75°.
isoButyl alcohol	0.810-0.815	0.72	30°-75°.
Butyl alcohol	0.800-0.805	0.70	30°-75°.
Propyl alcohol	0.771-0.776	0.77	30°-75°.
isoPropyl alcohol	0.759-0.791	0.50	30°-60°.

The results on the susceptibilities of water have been confirmed by Johner (*Helv. Phys. Acta*, 1930, iv, **3-4**, 238-280), and the magnitude of the change observed by him is identical with ours. It is to be noted that after examining a large variety of substances, we could find only water and a few aliphatic alcohols to possess the remarkable property of showing an increase in diamagnetism due to temperature. This phenomenon is not so general as the reverse phenomenon namely that of decrease in diamagnetism with temperature. Table II contains a brief resumé of the investigations on the subject by Abdul Azim, R. N. Mathur and M. B. Nevgi.

TABLE II.

Substance.	$-\chi \times 10^6$ .	% Change.	Range of temperature.
Nitrobenzene	0.498-0.471	5.4	20°-75°.
Toluene	0.730-0.710	2.66	20°-75°.
Chlorobenzene	0.640-0.606	5.26	20°-75°.
Iodobenzene	0.475-0.454	4.35	20°-75°.
Bromobenzene	0.483-0.458	4.80	20°-75°.
Aniline	0.700-0.666	4.81	20°-75°.

Similar results have been obtained with  $\alpha$ -bromonaphthalene, benzonitrile, ethylbenzene, xylene (*meta*), benzene, *pseudocumene* and *mesitylene*.

Table III gives a couple of examples of substances which show practically no change with temperature.

TABLE III.

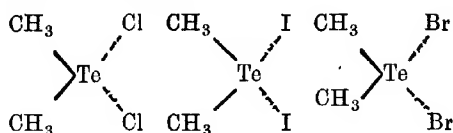
Substance.	$-\chi \times 10^6$ .	% Change.	Range of temperature.
<i>cyclo</i> Hexane.	0.810–0.808	0.24	20°–60.
Carbon tetrachloride	0.439–0.432	0.40	20°–60.

Substances of the type like water and the aliphatic alcohols show large variations of association and dissociation with temperature and it looks as if the change in magnetic properties is intimately connected with these changes. As a rule the aliphatic compounds show a much lesser change in diamagnetism with temperature than the corresponding aromatic compounds. In Table II, the largest decrease in diamagnetism observed is in the case of nitrobenzene, although  $\alpha$ -bromonaphthalene also shows a large decrease.

While no definite quantitative rule has yet been formulated, it is evident that the diamagnetism in aromatic compounds is very much more considerably influenced by temperature than that in the case of the aliphatic compounds. Evidently the benzene ring formation is important from the magnetic standpoint, as at least two other important facts seem to be correlated with the peculiar behaviour of aromatic substances: Firstly the aromatic compounds exhibit much larger magnetic double refraction and secondly they can be much more easily crystallised than the corresponding aliphatic compounds. These effects are certainly connected with the electronic structure of the aromatics.

From considerations shown above it is clear that the influence of temperature on diamagnetic substances is capable of yielding valuable information regarding their electronic configuration and their chemical constitution. As an interesting example of this may be quoted an investigation by Mr. T. K. Labiri in this laboratory on the influence of temperature on the magnetic properties of substances like dimethyltellurium diiodide, dimethyltellurium dibromide, dimethyltellurium dichloride and dimethyltellurium dinitrate prepared by Mr. Balwant Singh.

According to Sugden (*J. Chem. Soc.*, 1927, 1173; 1930, 229) the constitution of these substances is given by



where the dotted lines represent the single-electron bond whose parachor is about half that of the two-electron linkage.

Sidgwick (*Trans. Faraday Soc.*, 1923, 19, 469; *J. Chem. Soc.*, 1924, 125, 532) questions the possibility of a single-electron linkage and goes so far as to say that tellurium completes a decet instead of an octet in these compounds. According to G. N. Lewis and the magneto-chemical theory of L. Pauling the single electron bond ought to have a magnetic moment and even though the diamagnetism of the constituent halide and the methyl radicals may mask its paramagnetic effects, the temperature influence on its magnetic property should show a decrease in the paramagnetism of the single-electron bond and a consequent rise in diamagnetism of these substances. A preliminary examination of the dichloride by Lahiri reveals the fact that the change of  $\chi$  with temperature is negligible. This fact supports Sidgwick and throws doubt on Sugden's concept of a single-electron bond in the above compounds. Before final judgment can be pronounced, the effect of temperature on tellurium in various combined forms must however be investigated.

Reverting to the case of liquids which show an increase in the value of  $\chi$  with temperature, Van Vleck (*Phys. Rev.*, 1927, 29, 727; 1928, 31, 587) and Bitter (*Physikal. Z.*, 1929, 30, 497) have shown that

$$\chi = N(a + \frac{\mu^2}{3kT})$$

where  $N$  is the number of molecules per c.c.,  $T$  is the absolute temperature and  $a$  is a constant and the rest of the symbols have their usual significance. From this it follows that the electrically polarised molecules such as water, propyl and isopropyl and butyl and isobutyl alcohols will have an additional paramagnetic moment whose value will decrease with temperature. The diamagnetic susceptibility of such a molecule shall therefore tend to increase with rise of temperature. Johner has tried to quantitatively test this view on water molecules, but the observed increase between  $0^\circ$  and  $100^\circ$  is found to be ten times greater than what can be accounted for on the polarisation hypothesis. From this it is clear that a large

part of this increase is due to change in association; only a small part of this effect is due to the polarisation factor. Similarity in the order of increase in the diamagnetism of alcohols and water, in the values of boiling points of the alcohols and in their degrees of association prove beyond doubt the validity of this view.

The interesting case of liquids which show a decrease of  $\chi$  with temperature particularly noticeable in the case of aromatic compounds shows beyond doubt that orientating effects are more prominent in these liquids. This is further evident from the greater tendency of the aromatic compounds to crystallise than the corresponding aliphatic compounds. It is also significant to note that greater dipole moments have been found by Rolinski (*Physikal. Z.*, 1928, 29, 651-667) to be characterised by greater tendencies towards association which means that association is a factor which favours ease of crystallisation. Support to this view is obtainable from the experimental facts described above which show that temperature which disturbs the orientation and destroys the tendency towards crystallisation also decreases the dipole moment and the magnetic susceptibility in the case of aromatic compounds.

From all this it is clear that in aromatic compounds there is a crystallisation structure effect which contributes to the susceptibility and it is decrease in this part of diamagnetism which is mainly responsible for the observed decrease of  $\chi$  with temperature.

Table IV shows clearly the analogy between the influence of temperature on the thermal variation of the Cotton-Mouton constant and the change of susceptibility.

TABLE IV.

Substance.	Formulae.	Cotton-Mouton constant.	Temperature coefficient of Cotton-Mouton constant.	%Change of $\chi$ between 20°-75°.
Nitrobenzene	$C_6H_5NO_2$	100.0	$\frac{1}{138}$ (6.4-53.9)	5.4
Chlorobenzene	$C_6H_5Cl$	28.8	$\frac{1}{139}$ (5.2-55.1)	5.26
Bromobenzene	$C_6H_5Br$	25.7	$\frac{1}{144}$ (4.7-54.7)	4.80
Bromonaphthalene	$C_{10}H_7Br$	99.0	$\frac{1}{218}$ (5.7-52.4)	5.94
Pseudocumene	$C_8H_8(CH_3)_2$	28.0	$\frac{1}{143}$ (5.1-54.5)	1.85

Since magnetic birefringence, thermal variation of magnetic susceptibilities and ease of crystallisation in aromatic compounds seem to run parallel, it appears certain that the decrease of  $\chi$  in these compounds is due to disturbances in crystalline alignments or orientations brought about as a result of heating.

It is interesting to point out here that in Prof. Cotton's laboratory it has been shown that liquid crystals which are midway between liquid and crystalline states show much larger magnetic birefringence than in nitrobenzene.

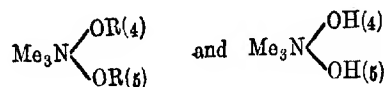
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## Studies in Constitution of Optical Isomers Containing Pentavalent Nitrogen and Geometrical Inversion.

BY PANCHANAN NEOGI.

The constitution of optical isomers containing pentavalent nitrogen has been a subject for debate for over half a century. Van't Hoff, as early as 1878, himself postulated a space representation for nitrogen, the nitrogen being at the centre of a cube, the five valencies being directed to five of its eight corners. This, however, makes the space representation a highly unsymmetrical one as only five out of eight corners are occupied. With a view to make it more symmetrical Wilgerodt in 1890 (*J. pr. Chem.*, 1890, **41**, 291) suggested a double tetrahedron formula for pentavalent nitrogen. The number of possible isomers of the type  $\text{NA}_3\text{BX}$ ,  $\text{NA}_2\text{BCX}$ ,  $\text{NABCDX}$ , however, according to both the configurations remains the same. Bischoff (*Ber.*, 1908, **41**, 1197) found out that the number of possible isomers according to both Van't Hoff and Wilgerodt's formulae was disproportionately large, and proposed a pyramid formula for pentavalent nitrogen. This formula was accepted by a large body of chemists interested in stereochemical work for a long length of time as giving the least number of isomers containing nitrogen, resolvable as well as non-resolvable.

When, however, Werner enunciated his ideas about co-ordination compounds, he showed that  $\text{NH}_4$  forms a compact co-ordinated complex and the fifth bond is outside the co-ordination group  $[\text{NH}_4]\text{Cl}$ . This naturally suggests that the fifth bond of nitrogen is differently situated from the remaining four bonds and this fact should be represented in any system of space formulae for nitrogen. Meseinheimer (*Annalen*, 1913, **397**, 273) was able to furnish experimental proof of this fact by showing that



are isomeric and give rise to different products on heating. He

therefore suggested a single tetrahedron representation of nitrogen with the fifth bond somewhere outside it.

This subject attracted the attention of Neogi who, in a paper published in 1919 (*J. Amer. Chem. Soc.*, 1919, **41**, 622) showed that a single tetrahedron with the nitrogen atom at the centre and the fifth bond outside it but linked to the nitrogen with one bond through one face, should substitute Van't Hoff's cubical, Wilgerodt's double tetrahedron and Bischoff's pyramid formulae for nitrogen. It is the purpose of this paper to give a resumé of the principal points in favour of this formula and also to deal with the literature which has appeared after the publication of this paper.

The essential facts, which include later work in support of the single tetrahedron formula, are the following:

(1) The number of isomers, resolvable as well as non-resolvable, of organic ammonium compounds as deduced from the first three formulae is extremely large, and careful experiments by many chemists have systematically failed to yield any of these isomers. The following table will show at a glance that while the discrepancy between theory and experiment regarding the number of possible isomers of the type  $NA_3BX$ ,  $NA_2BCX$ ,  $NABCDX$  is so glaring in the case of the first three formulae, the number of possible isomers obtained experimentally and actually resolved exactly tallies with the deductions from the single tetrahedron formula.

			$NA_3BX$ .	$NA_2BCX$ .	$NABCDX$ .
Van't Hoff's cube	...	...	2	3†	4‡
Wilgerodt's double tetrahedron		...	2	3†	4‡
Bischoff's pyramid	...	...	nil	2†	3‡
Single tetrahedron	...	...	nil	nil	1†
Experiment	...	...	nil	nil	1†

(2) As the number of isomers with only one nitrogen atom is so large it is only natural that the number of optical isomers of an organic compound containing one carbon and one pentavalent nitrogen atom or two pentavalent nitrogen atoms as predicted by the first three formulae would be absurdly large, whilst according to the single tetrahedron formula there will exist two optically active isomers of a compound containing either one carbon atom joined to a pentavalent

† One divisible into optical isomers.

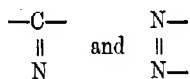
‡ Each " " "

nitrogen atom or two pentavalent nitrogen atoms. This fact has been experimentally confirmed by Widekind and Ney (*Ber.*, 1912, **45**, 1912), Wedekind and Bandau (*Annalen*, 1913, **401**, 326; 1914, **404**, 334) and others.

(3) The fifth bond of nitrogen has definitely been proved by Mesienheimer to be differently situated from the remaining four bonds and the failure on the part of Van't Hoff, Wilgerodt and Bischoff to recognise this fact led them to enunciate their respective formulae. Jones (*J. Chem. Soc.*, 1905, **87**, 1728) attempted to show that the pyramid formula was capable of explaining the existence of only two optical isomers of the type NABCDX and the non-existence of any isomers of the compound of the type  $\text{NA}_2\text{BCX}$  on the basis of the pyramid formula. This argument has conclusively been shown by Neogi (*loc. cit.*) to be erroneous and he notes with satisfaction that J. B. Cohen has omitted the entire argument of Jones from the 1928 edition of his well known treatise on Organic Chemistry which was incorporated in the earlier editions of his book.

On the question of the non-equivalence of the fifth bond the first apparent conflict came from the discovery by Schlenk (*Ber.*, 1917, **50**, 274, 823) of tetramethylbenzyl-ammonium,  $\text{NMe}_4 \cdot \text{CH}_2\text{C}_6\text{H}_5$  in which the benzyl group takes the place of negative halogen. Schlenk himself, however, has shown that this compound when dissolved in pyridine conducts electricity and hence, as has justly been pointed out, the benzyl group is presumably ionisable as an anion in the same manner as the halogen atom in the quarternary ammonium salts. The single tetrahedron formula may thus figuratively be represented to have successfully negotiated the first hurdle or obstacle that has arisen in its path.

(4) The passage of trivalent nitrogen to pentavalency has been represented by Neogi in the following diagrams. It is to be remembered that all attempts at resolution of an organic compound containing trivalent nitrogen have failed and it is apparent that trivalent nitrogen has a plane configuration. The existence of geometrical isomers containing



systems, however, shows that trivalent nitrogen is also capable of assuming a space representation as well, specially when joined by double bonds.



Hantzsch and Werner postulated a full tetrahedron configuration for trivalent nitrogen with N at the apex and the three bonds acting along the three edges emanating from the apex. This explains the geometrical isomerism of oximes, diazo and other compounds containing a carbon—nitrogen (trivalent) or two trivalent nitrogen systems but does not indicate the ready passage of trivalent to pentavalent nitrogen by addition or oxidation. Moreover, Meseinheimer (*Annalen*, 1911, 385, 117) has shown that amine oxides of the type  $abcN=O$  can be resolved into optical isomers. None of the earlier three configurations gives a symmetrical explanation of the isomerism of the amine oxides and even with the pyramid formula the resulting configuration will require the formation of three asymmetric isomers each capable of resolution into active varieties which, however, do not exist.

With a view to explain both the geometrical isomerism of compounds containing trivalent nitrogen as well as passage of trivalent nitrogen to pentavalency and also to explain the optical isomerism of amine oxides, Neogi (*loc. cit.*) has introduced the conception of what has been called "in-tetrahedron" and suggested the following theory about its space representation.

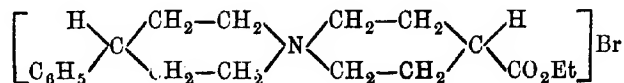
(a) Ordinarily trivalent nitrogen has a plane configuration.

(b) In compounds containing  $C=N$  or  $N=N$  systems the three bonds of nitrogen might be bent along the edges of an "in-tetrahedron," the nitrogen atom occupying its apex.

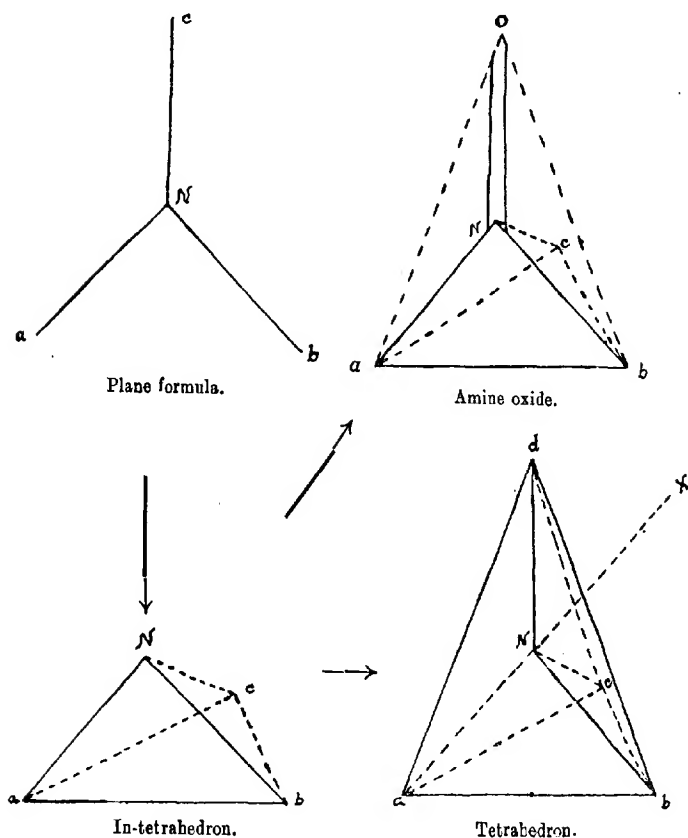
(c) When trivalent nitrogen passes to pentavalency the complete tetrahedron is formed. The passage of trivalent nitrogen to pentavalency in ammonium compounds and amine oxides has been diagrammatically represented on the next page.

In "in-tetrahedron" the nitrogen atom occupies the central apex and in the complete tetrahedron it occupies the centre. In the amine oxides the bonds  $d$  and  $x$  together bind the divalent oxygen atom.

(5) The single tetrahedron theory has successfully crossed the second hurdle when in 1925 Mills and Warren (*J. Chem. Soc.*, 1925, 127, 2507) resolved



into active isomers. This experiment is a direct proof in favour of the single tetrahedron formula.



With pyramidal arrangement the four radicals attached to the outlying carbon atoms of the ring are brought into the same plane as the nitrogen atom forming a plane of symmetry thus excluding possibility of resolution. This is therefore excluded. On the other hand, the single tetrahedron arrangement would require the two rings to exist in planes at right angles to each other and so produce asymmetry and hence, the possibility of resolution of the compound into optical isomers becomes manifest.

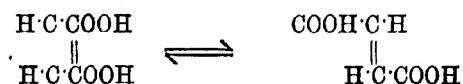
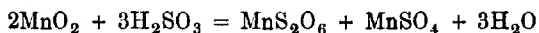
(6) Loring in his treatise ("Atomic Theories," p. 139) has shown that the single tetrahedron formula accords with the electronic conception of the structure of the nitrogen atom as adumbrated by Lewis-Langmuir. This upholding of the tetrahedron structure of the nitrogen atom by the octet valence theory is a positive proof of the validity of the former.

It will thus be seen that more recent work by different investigators has so far substantiated the correctness of the single tetrahedron formula.

### *Geometrical Inversion.*

Neogi and co-workers (Neogi and Chatterjee, *J. Indian Chem. Soc.*, 1928, **5**, 279; Neogi and Mitra, *ibid.*, 1929, **6**, 969) have been able to effect geometrical inversion by a novel method. They have shown that maleic acid may be converted into fumaric acid in the presence of the exothermic reaction that occurs when  $\text{SO}_2$  is passed through precipitated  $\text{MnO}_2$  held in suspension. The products of the reaction between  $\text{SO}_2$  and  $\text{MnO}_2$  are manganous dithionate and manganous sulphate. It was shown by the authors that neither the reactants nor the products of the reaction are themselves capable of effecting the inversion. The conclusion therefore irresistibly follows that the inversion has been effected in the presence of the exothermic reaction itself.

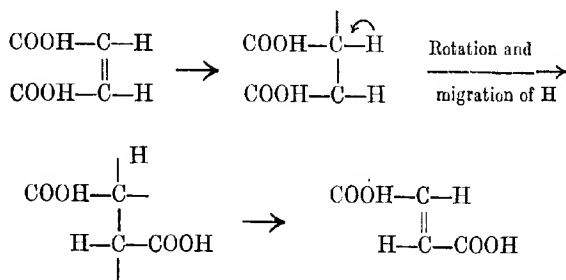
A similar phenomenon was observed by Skraup (*Monatsh.*, 1891, **12**, 102), who showed that maleic acid is capable of being transformed into fumaric acid in the presence of the reaction between  $\text{H}_2\text{S}$  and  $\text{SO}_2$ , though the reactants as well as the products of the reaction themselves are not capable of effecting the inversion. Neogi and co-workers (*loc. cit.*) have extended this phenomenon to the conversion of citraconic to mesaconic acid though it has been found that all exothermic reactions do not effect the inversion. They have named such reactions as "resonance reactions" which have been defined as "a chemical reaction which takes place in the midst of another chemical reaction but not in the presence of any of the reactants singly nor in the presence of the products of the latter reaction." A resonance reaction is very different from an "induced reaction" discovered by Kessler and others as there is no "acceptor," "actor" or "inductor." The two parallel reactions in the transformation of maleic to fumaric acid in the presence of manganese dioxide and sulphur dioxide are the following:



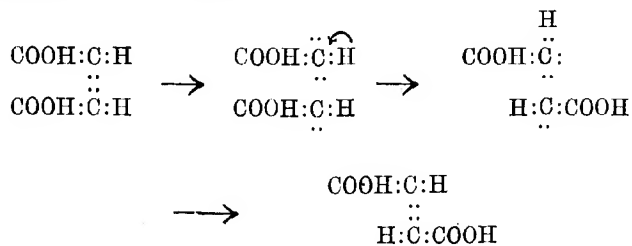
Geometrical inversions have, up to this time, been the only instances of resonance reactions.

Whilst studying the mechanism and the cause of geometrical inversion Neogi (*Chem. News*, 1930, Aug., 30) has advanced a theory which seeks to explain geometrical inversion on new lines. He discards Wislicenus' theory of formation of intermediate additive derivatives and shows Cohen's explanation as given in his Treatise on Organic Chemistry to be faulty and postulates migration of one hydrogen atom or the most labile radical accompanied by rotation of one carbon atom after disruption of the double bond as the most satisfactory method of explaining the mechanism of geometrical inversion.

The mechanism of inversion of maleic to fumaric acid according to Neogi is given below :



On the electronic hypothesis, the transformation would be represented in the following manner :



With a view to emphasise the hypothesis that geometrical inversion is occasioned by the rotation of carbon atoms owing to the instability of the double bond accompanied by the migration of a hydrogen atom or a similar group, Neogi (*loc. cit.*) has coined the word "rotaversion" to connote geometrical inversion and 'rotamerism' to denote geometrical isomerism.

As regards the rationale of the process he summarises the conditions under which the labile variety is usually transformed into the stable one and *vice versa* as follows :

Agents.	Conversion of labile to stable variety.	Conversion of stable to labile variety.
Low frequency radiations		High frequency radiations
	(1) Heat	(1) Higher temperature
	(2) Light	(2) Ultraviolet rays
	Catalytic agents	
	Exothermic reactions	

A labile variety *ipso facto* possesses greater energy content than the stable variety so that ordinarily the former is converted to the latter, and special agencies such as ultraviolet rays or higher temperature can alone transform the stable to the labile variety by the supply of energy in a suitable form. The action of catalysts, exothermic reactions, heat and light, etc., initially increases the energy content of the labile variety, thus activating it and increasing its velocity of transformation to the stable variety and necessarily by the liberation of a certain amount of energy. The molecules of the labile variety are thus activated and ultimately form the stable variety.

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## Observations on the Chemistry of Vitamins B<sub>1</sub> and B<sub>2</sub>.

BY BIRES CHANDRA GUHA.

The researches of Goldberger and his collaborators (Goldberger and Tanner, *U. S. Public Health Rep.*, 1924, **39**, 87; Goldberger, Wheeler, Lillie and Rogers, *ibid.*, 1926, **41**, 297; Goldberger and Lillie, *ibid.*, 1926, **41**, 1025) established the fact that the so-called "vitamin B," which was originally considered to be a single chemical individual by a majority of biochemists, consisted in reality of at least two different substances. These were subsequently termed vitamins B<sub>1</sub> and B<sub>2</sub> according to the English system of nomenclature, and B (or F) and G, according to the American system and were considered to be the curative (and preventive) agents of "polyneuritis" and "pellagra" respectively. Subsequent work, however, (Reader, *Biochem. J.*, 1929, **23**, 689; Guha, *J. Soc. Chem. Ind.*, 1930, **49**, 850; Guha, *Biochem. J.*, 1931, **25**, 960; Hunt, *J. Biol. Chem.*, 1929, **79**, 723) indicates that there are other hitherto unrecognised factors which are also necessary for the normal nutrition of the rat. The work of Williams and Waterman (*J. Biol. Chem.*, 1928, **78**, 311), Guha (*J. Soc. Chem. Ind.*, 1929, **48**, 1248) and Carter, Kinnersley and Peters (*Biochem. J.*, 1930, **24**, 1832, 1844) also indicates that there are factors, besides the known vitamins, which are necessary for avian nutrition.

These observations have naturally led to renewed efforts at the isolation of the different vitamins. The chemistry of vitamins B<sub>1</sub> and B<sub>2</sub> is dealt with in the present paper.

### Vitamin B<sub>1</sub>.

The claims of the earlier workers in this field, Funk, Abderhalden, Suzuki and others to have isolated the "anti-neuritic" "vitamin B" have since been disproved. Among the more recent workers in this field, Jansen and Donath (*Proc. K. Akad. Wetenschap. Amsterdam*, 1926, **29**, 1390) have announced the isolation of the vitamin in a crystalline form from rice-polishings. They considered the vitamin to be a glyoxaline derivative. Williams, Waterman and Gurin

(*J. Biol. Chem.*, 1930, **87**, 559) were not able to obtain the same crystalline material from rice-polishings by following Jansen and Donath's procedure. The subsequent work of Jansen, Kinnersley, Peters and Reader (*Biochem. J.*, 1930, **24**, 1824) is stated to indicate however, that the material obtained by Jansen and Donath contained both vitamins B<sub>1</sub> and B<sub>2</sub> (a more recently discovered B-factor).

A fractionation was carried out by Guha and Drummond (*Biochem. J.*, 1929, **23**, 880), in which wheat embryo was employed and a method involving acid alcoholic extraction, adsorption by fuller's earth, fractionation by silver nitrate—baryta at different hydrogen ion concentrations, precipitation with phosphotungstic acid, followed by fractionation with platonic and gold chlorides was used. The semi-crystalline material obtained proved to be active for the growth of rats in a daily dose of 0.015 mg. and curative of 'polyneuritis' in pigeons in a dose of 0.005 mg. This activity appeared to be of the same order as that of Jansen and Donath's product, although it was admittedly impure. A similar process of fractionation applied to brewer's top yeast yielded a less active product (Guha, *Biochem. J.*, 1931, **25**, 931). The absorption spectra of certain vitamin B<sub>1</sub> concentrates were studied. A concentrated yeast preparation exhibited definite absorption in the region of 260 $\mu$ . But a very potent concentrate, kindly supplied by Prof. J. C. Drummond, failed to show this absorption band (Guha, *Biochem. J.*, 1931, **25**, 931). Windaus, Tschesche, Ruhkopf, Laquer and Schultz (*Z. Physiol. Chem.*, 1932, **204**, 123) have recently claimed to have isolated vitamin B<sub>1</sub> from yeast, which they have found to be a sulphur containing nitrogenous compound, exhibiting absorption in the region of 260 $\mu$ . It is, however, uncertain how far absorption in this region is specific for vitamin B<sub>1</sub>, although Windaus claims it to be so. Van Veen (*Z. Physiol. Chem.* 1932, **208**, 125) has also described the isolation of vitamin B<sub>1</sub> crystals from rice-polishings, which resembles Windaus' preparation from yeast. It is, however, still premature to discuss the purity of these preparations.

It has been supposed for a long time that vitamin B<sub>1</sub> is a base—a supposition, which is based on the indirect evidence that the fractionation methods used for the isolation of vitamin B<sub>1</sub> are similar to those usually employed for the isolation of natural bases. Conclusive evidence on this point has, however, been brought forward recently (Birch and Guha, *Biochem. J.*, 1931, **25**, 1891). Vitamin B<sub>1</sub> has been shown to migrate towards the kathode even

at pH 8.6 in electrodialysis experiments applied to potent vitamin B<sub>1</sub> concentrates, showing that it is a fairly strong base.

#### *Vitamin B<sub>2</sub>.*

Since the recognition of the fact that both vitamins B<sub>1</sub> and B<sub>2</sub> are required to produce growth in young rats subsisting on a diet deficient in "vitamin B", much evidence has been brought forward to show that they are chemically and physiologically distinct (Guha, *Nature*, 1931, **127**, 594; *Biochem. J.*, 1931, **25**, 945). The relative heat-stability of vitamin B<sub>2</sub> was originally noted by Goldberger—an observation which has since been generally confirmed (Hassan and Drummond, *Biochem. J.*, 1927, **21**, 653; Narayanan and Drummond, *ibid.*, 1930, **24**, 19). It has, however, been found recently that the behaviour of vitamin B<sub>2</sub> to heat varies according to the sources, from which it is extracted. Its stability appears to be related to the presence of other materials in the preparation tested. Thus certain commercial preparations from yeast and liver appeared to be more stable than aqueous extracts obtained from fresh ox liver and yeast (Guha, *Biochem. J.*, 1931, **25**, 945). Fresh preparations from yeast have also been found to deteriorate in their vitamin B<sub>2</sub> content by Williams, Waterman and Gurin (*J. Biol. Chem.*, 1929, **83**, 321), and by Chick and Roscoe (*Biochem. J.*, 1930, **24**, 105).

It has been observed that a commercial preparation of liver extract, used for pernicious anaemia (Ely Lilly's liver extract, No. 343) is very potent in vitamin B<sub>2</sub>, Guha, *Lancet*, 1931, i, 864). A general chemical study of vitamin B<sub>2</sub> in this preparation (Guha, *Biochem. J.*, 1931, **25**, 945) has revealed that it is not precipitated by picric acid, benzoyl chloride, phosphotungstic acid and flavianic acid. Nitrous acid neither precipitates nor inactivates it. Lead acetate and silver nitrate precipitate it partially. Esterification leaves about 40% of the vitamin in the non-esterified fraction, the esterified fraction being inactive. It is not attacked by trypsin. Norite charcoal adsorbs the vitamin effectively at the normal pH (4.6) of the aqueous extract of the liver concentrate. It was not, however, possible to elute the vitamin well by different alcohols, aqueous ethyl alcohol at different hydrogen ion concentrations or by dilute saponin (at the time of writing it has been found that concentrated



HCl elutes the vitamin from animal charcoal, with which the vitamin can be adsorbed). On the basis of the present evidence the vitamin may be provisionally considered to be probably neither a base, acid nor peptide but a neutral substance. Preliminary electrodialysis experiments applied to a solution of the liver concentrate appear to support this tentative conclusion. The vitamin has been found to be stable to treatment with sulphur dioxide, hydrogen peroxide and ozone under the conditions studied.

The problem of the isolation of vitamins B<sub>1</sub> and B<sub>2</sub> has not yet been settled, though their isolation in a pure state is not probably remote.

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## Einige Bemerkungen über die quantitative Ermittlung sehr kleiner Stoffmengen.

VON FRIEDRICH EMICH.

Die Genauigkeit einer quantitativen Bestimmung ist bekanntlich unter sonst gleichen Umständen um so höher, je grösser das Molekulargewicht der Bestimmungsform gewählt werden kann. Wir brauchen nur an das Beispiel des phosphormolybdänsauren Strychnins zu erinnern, das bei der Bestimmung des Phosphors mit dem "Faktor"  $1/89$  in die Rechnung eingeht, um die Wichtigkeit des obigen Gedankens zu beweisen.\* Indess handelt es sich in diesem Falle nur um ein Teilgebiet eines grösseren Fragenkomplexes, bei dem das Bestreben des Experimentators dahin geht, die Einheit, mit der die Bestimmungsform gemessen wird, möglichst klein zu gestalten. Das kann eben in sehr verschiedener Weise geschehen, z. B. auch dadurch, dass man die Bestimmungsform mittels geeigneter Prozesse in eine Materie oder in einen Zustand überführt, der eben die feinere Messbarkeit ermöglicht. Damit sind u. a. auch die optischen Methoden (Spektrometrie, Colorimetrie etc.) unter diesen Gesichtspunkt gebracht.

In der vorliegenden kleinen Mitteilung, die Sir Prof. Dr. Prafulla Chandra Ray anlässlich seines siebenzigsten Geburtstages gewidmet ist, möchte ich auf einige Möglichkeiten solcher Art hinweisen, die meines Wissens bisher keine Rolle in der Mikroanalyse gespielt haben. Ich muss nur hinzufügen, dass keines der angedeuteten Verfahren experimentell geprüft werden konnte; es sind eben nur Vorschläge, die wie ich glaube, in solchen Fällen in Betracht kämen, in denen man gern ein Opfer an Zeit bringt, um dafür mit einem Minimum an Material auszukommen.

\* Vielleicht wäre es zweckmässiger, anstatt des Wortes "Faktor" den reziproken Wert anzuwenden, den man etwa die "Vergrösserungszahl" nennen könnte. Vergl. meinen Vortrag über Mikrochemie (*Z. angew. Chem.*, 1931, **44**, 725 oder Mikrochemie 1932, **10**, 467) woselbst derartige Verfahren als "Multiplikationsverfahren" erwähnt worden sind.—Wie schön wäre es, wenn man Wasserstoff als Iodwasserstoff wägen könnte!

† Dies ist deshalb nicht möglich, weil ich zur Zeit kein Institut besitze.

## I.

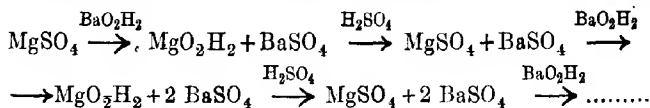
Man kann sich die Aufgabe stellen, einen zu bestimmenden Stoff solchen stoechiometrischen Umwandlungen auszusetzen, die sein Gewicht nach und nach (bis zu entsprechender Messbarkeit) erhöhen. Zwei einfache Beispiele mögen dies veranschaulichen.

(a) Es sei Silbersulfat in unwägbarer Menge gegeben. Dann kann ich es durch Verreiben mit Chlorbariumlösung in ein Gemisch von Chlorsilber und Bariumsulfat verwandeln, das nach dem Waschen und Abrauchen mit Schwefelsäure Silbersulfat und Bariumsulfat ergibt. Dieses Gemisch kann wieder mit Chlorbarium behandelt werden u.s.w. So liefern (in abgerundeten Zahlen) 312 T.  $\text{Ag}_2\text{SO}_4$ , 545 T.  $\text{Ag}_2\text{SO}_4 + \text{BaSO}_4$ , dann 778 T.  $\text{Ag}_2\text{SO}_4 + 2 \text{BaSO}_4$ , usw. Die "Vergrößerungszahl" ist nach  $n$ -maliger Wiederholung

$$\frac{312 + 233 n}{312},$$

also z. B. nach zehnmaliger Wiederholung des Verfahrens 8·39, d.h. man hat annähernd schon den Uebergang zur nächsten Dezimalstelle erzielt.

(b) Günstiger lägen die Verhältnisse, wenn etwa Magnesiumsulfat gegeben wäre, wobei folgendes Verfahren einzuschlagen wäre:



Nach zehnmaliger Wiederholung ist die Vergrößerungszahl 20·4. Weitere Beispiele für diese Methodik, die an die Verstärkungsverfahren der Photographie erinnert, wären unschwer anzugeben.

## II.

(a) Ein Beispiel anderer Art. Aus einer unwägbaren Menge von Calciumkarbonat könnte die Kohlensäure durch Erhitzen ausgetrieben und von einem Absorptionsmittel aufgenommen werden, das natürlich noch keine nachweisbare Gewichtszunahme erführe. Wenn ich aber den Aetzkalk wieder in Karbonat verwandle und die angegebenen Prozesse wiederhole, könnte ich durch ein richtiges "Multiplikationsverfahren" die Kohlensäure schliesslich doch zur Wägung bringen. Aehnlich könnten bei abwechselnder Reduktion und Oxydation unwägbare Wassermengen der Bestimmung zugeführt und damit z.B. eine *kupferspur* ermittelt werden.

(b) Reinstes Kohlendioxyd könnte im geschlossenen Raum durch Erhitzen mit Kohle in Kohlenoxyd verwandelt werden. Wird dieses wieder Oxydiert und das Verfahren fortgesetzt, so ergeben sich bei zehnmaliger Reduktion und Oxydation aus einem Molekül Kohlensäure



d. h. die Vergrößerungszahl beträgt bei zehnmaliger Wiederholung  $2^{10} = 1024$ .

Die Methode müsste folgerichtig als "Potenzierungsverfahren" bezeichnet werden.

Die Apparatur denke ich mir so, dass der (Reduktions-) Kohlenstoff als elektrisch zu erhitzender Faden, das (oxydierende) Kupferoxyd als gleichfalls elektrisch zu erhitzender oxydierter Kupferdraht angewandt werden würde. Es wäre nicht schwer, die abwechselnden Oxydationen und Reduktionen automatisch einzuleiten, so dass die Apparatur ohne besondere Beaufsichtigung arbeiten könnte.

Auf solcher Basis könnten Kohlenstoffbestimmungen unter Anwendung von z.B. einigen Tausendstelmilligrammen Substanz (gewogen auf der elektromagnetischen Mikrowaage; E. Wiesenberger, *Mikrochemie*, 1931, 10, 10) durchgeführt werden.

### III.

#### *Methoden der Gasmessung.*

(a) Besonders einfach gestaltet sich die Ermittlung von Metallmengen nach dem Verfahren, das grundsätzlich auf die Thalliumbestimmung nach Georg Neumann (*Ber.*, 1888, 21, 356 und *Z. anal. Chem.*, 1887, 26, 531) zurückgeht. Sie besteht darin, dass man das Metall nach seiner elektrolytischen Abscheidung in verdünnter Schwefelsäure auflöst und den freigewordenen Wasserstoff misst. Wird hierbei etwa ein Mikroazotometer verwendet (Neumann benützte sein "Hydrometer"), so ergibt sich beim Thallium rund eine Genauigkeit von 0.02 mg., beim Zink etwa eine von 0.003 mg. D. h. man kann im zweiten Fall beinahe die Genauigkeit der Kuhlmannwaage erreichen (ohne das Instrument anwenden zu müssen).

(b) Eine weitgehende Verminderung der kleinsten ermittelbaren Menge wird erzielt, wenn man den Wasserstoff als Bläschen mikrometrisch nach A. Krogh (*Skand. Arch. Physiol.*, 1908, 20, 279) misst. Beispielsweise wägt ein Wasserstoffbläschen von 0.1 mm.

Durchmesser  $4 \times 10^{-5} \gamma^*$  entsprechend einer Zinkmenge von  $1.4 \times 10^{-3} \gamma$ . Inwieweit sich bei noch kleineren Bläschen eine Aenderung der Absorption störend bemerkbar machen würde, müssten besondere Versuche (Berechnungen ?) lehren. Krogh hat noch mit Bläschen von 0.1 mm. Durchmesser gearbeitet \*\* und eine Genauigkeit von 1-2% erzielt.

(c) Auch die Messung von kleinen Mengen Kohlensäure und Stickstoff scheint aussichtsvoll. F. Paneth hat Helium in Mengen von  $10^{-5} \text{ cm}^3$  auf 1% genau gemessen; dem würden z. B.  $5 \times 10^{-5} \text{ mg. Calcium karbonat}$  entsprechen, wenn die Kohlensäure ausgetrieben und gemessen werden würde. Die Messung kleiner Stickstoffmengen würde eine Art Dumas-Verfahren unter Anwendung von einigen  $\gamma$  Substanz ermöglichen. Die Verbrennung wäre z. B. im Vakuum oder in abgeschlossener Kohlensäureatmosphäre vorzunehmen. Der Nutzen, den die biologischen Wissenschaften aus den angedeuteten Verfeinerungen der Mikro-Elementaranalyse ziehen könnten, würde voraussichtlich die aufzuwendende Mühe (die ich nicht gering einschätze) lohnen.

#### IV.

Eine weitere Möglichkeit, sehr kleine Mengen von z. B. Wasserstoff oder einem anderen Reduktionsmittel zu bestimmen, bestünde darin, dass man es auf eine geeignete Edelmetallsalzlösung einwirken liesse. Das reduzierte Metall wäre zu einem Kügelchen zusammenzuschmelzen und mikroskopisch nach Vikt. Goldschmidt und Fritz Haber auszumessen. Einem Goldkügelchen von  $10 \mu$  Durchmesser entspräche eine Wasserstoffmenge von  $1.5 \times 10^{-4} \gamma$ , bzw.  $1.5 \times 10^{-6} \text{ cm}^3$ .

#### V.

Wie weit die praktische Durchführung der hier angedeuteten Verfahren auf Schwierigkeiten stossen würde, ist nicht vorherzusagen; ich glaube aber, dass sie sich überwinden liessen. Die wichtigste Frage wäre natürlich die nach den Fehlerquellen. Sie zu ermitteln, müssten Blindversuche und Versuche mit grösseren Mengen ausgeführt werden, bei denen die "Vergrösserungszahl" überprüft werden würde.

GRAZ, 1932.

1  $\gamma$  = 0.001 mg.

\*\* Herr Prof. Dr. Bendorff, den ich zurate zog, machte mich gütigst auf die Abhandlung von Heinr. Mach, Ueber die Diffusion und den Uebergang von Gasen in Flüssigkeiten, 1. Mitt., Sitzungsber. Akad. Wiss. Wien, math.-naturw. Kl. II a, 1929, 138, 7, Heft aufmerksam.

## The Mechanism of the Swelling of Gels.

By K. KRISHNAMURTI.

It is well known that many of the lyophilic gels absorb liquids and undergo a corresponding increase in volume. This phenomenon is called the 'swelling of gels'. The amount of the liquid taken up depends upon the nature of the gel and the liquid in contact with it. In general, colloids the molecules of which are of a polar character readily swell in polar liquids; whereas non-polar colloids (*e.g.*, rubber) imbibe liquids which are of a non-polar character (Whitby and others, *Colloid Symp. Monograph*, 1928, **6**, 235).

The problem of the swelling of gels has been the subject of a great deal of research, and still there does not appear to be any clear agreement between the views of different workers regarding the mechanism of the process. The different theories that have been put forward by various investigators may be briefly summarised as follows (Bartell and Sims, *J. Amer. Chem. Soc.*, 1922, **44**, 289):

(1) *Capillary theory* which assumes that the swelling is due to the passage of the liquid through the capillaries of the gel, caused by a difference in surface tension between the solvent and the solution.

(2) *The osmotic theory* assumes that the passage of the liquid into the gels is caused by a difference in osmotic pressure between the external and the internal solutions. This view appears to be the one held by several investigators, specially in the case of substances like gelatin.

(3) According to the *colloid-chemical theory* (Fischer, Alexander's *Colloid Chemistry*, Vol. II, 235) as suggested by Fischer, the swelling of gels is connected with the hydration of the 'colloidal cells.'

(4) The so-called *repulsion theory* (Tolman, *J. Amer. Chem. Soc.*, 1918, **40**, 246) assumes that the colloidal particles become charged with electricity of the same sign, which gives rise to repulsive forces between the particles. Hence the gel tries to distend. In the first place, this theory is only applicable to gels in contact with electrolytes. Secondly, it may be pointed out that isoelectric gelatin swells quite appreciably in pure water, and even when the charge of the particles does increase in contact with acids, swelling increases only up to a certain point, beyond which it diminishes, though the charge

increases (Ghosh, *J. Chem. Soc.*, 1928, 711). Thus the charge of the colloidal particles is not the only one factor to be considered, though in certain cases it plays an important part.

(5) Katz (*Koll. Chem. Beih.*, 1917, 9, 1) put forward the view that the swelling of gel is to be regarded as the formation of a solid solution of the imbibed liquid in the gel. He came to this conclusion from the striking similarity between the swelling of gels and the formation of ideal concentrated solutions.

The above are the main theories put forward by previous workers. The gels exhibit such a great variety both in their nature and their manner of formation, that it is not possible to extend any single theory of swelling to all the different cases.

The swelling of gelatin in the presence of electrolytes has been thoroughly investigated by Proctor and Wilson (*cf.* Bogue's "Colloidal behaviour," 1924, p. 1), and Loeb (Loeb, "Proteins and colloidal behaviour," 1922). They have come to the conclusion that the swelling of gelatin in acids, bases and salt solutions is connected with the Donnan equilibrium, and that it is due to the osmotic pressure of the ions of the electrolyte inside the gel. But, it is also known that isoelectric gelatin swells appreciably even in pure water. This evidently is not connected with the Donnan equilibrium. To explain this Northrup and Kunitz (*J. Gen. Physiol.*, 1926, 10, 161) have assumed that the block of isoelectric gelatin is a network consisting of threads of a substance insoluble in cold water, and holding in its meshes a solution of a soluble form of gelatin. So when the block of gelatin is immersed in water the internal solution exerts osmotic pressure and consequently, water is taken in until the osmotic pressure is equalised by the elastic force of the network. The main difficulty with regard to this view is that we have to assume the presence of a soluble and insoluble form in every material which is capable of swelling in liquids other than electrolytes.

Recent work of the author (Krishnamurti, *Proc. Roy. Soc.*, 1929 **A**, 122, 76; 1930, **A**, 129, 490) on the scattering of light in agar and gelatin gels clearly indicates that these systems contain colloidal micelles which act as units. None of the existing theories says anything about the changes in these micelles during swelling. It was therefore felt that a careful examination of the changes in light-scattering during the swelling of gels would reveal the changes in the size of these micelles. The present investigation deals with this.

If a piece of gelatin be immersed in water, it becomes opalescent (Krishnamurti, *Nature*, 1929, 123, 242). This can be clearly noted when the swollen piece is illuminated by a strong beam of light and viewed against a dark background. The gel used for the determination of the changes in light-scattering during swelling was obtained by slowly drying a 2 per cent. gelatin gel of  $p_H$  3 in a desiccator for a few months when its concentration was found to be 20 per cent. Small quantities of water were added at a time to this gel, and it was left over until equilibrium was attained. This could be tested by determining the intensity of the scattered light at different parts of the gel (usually the top, middle and bottom layers). The final value of the "Tyndall intensity" was that obtained when the readings in the three different portions of the gel, were identical. The results are given in Table I.

TABLE I.

Weight of gel.			Intensity of scattered light. (Benzene = 1).
3.00	...	...	... 67.7
5.64	...	...	... 73.3
7.86	...	...	... 67.6
12.54	...	..	... 48.9
16.40	...	...	... 42.9

It can be seen from the above data that the intensity of the scattered light increases at first and then diminishes as swelling proceeds. It may be interesting to point out that in the earlier stages, *i.e.*, when the amount of water added was small, equilibrium was reached very quickly, whereas this process was much slower during the later stages when the amount of water added was large. In fact it takes about a fortnight in the later stages.

These observations appear to the author to provide a basis for the mechanism of swelling of gels. Swelling occurs as a result of imbibition of the solvent by the gel. We have to distinguish between two kinds of imbibition: (1) That in which the solvent is actually taken up inside the structure of the gel micelles. This part is held firmly by the molecules constituting the micelle owing to *forces which are probably chemical in nature*, and causes an increase in the volume of the micelle and hence an increase in the light-scattering capacity of the gel. This process stops when a certain limit is reached depending



upon the cohesion between the molecules constituting the micelle. (2) The solvent which is still further taken into the gel remains in the intermicellary space, thus causing a dilution of the gel, and hence a diminution in its light-scattering capacity. The opalescence observed at first when a dry piece of gelatin is immersed in water is probably caused by the water penetrating into the gelatin piece and making the system heterogeneous.

The above view is in complete harmony with the results obtained by the author, and receives further support from the observations of other investigators. Thus it is well known that most of the water that is absorbed by gelatin during swelling is given up again in an atmosphere saturated with water vapour. But, when we reach a water content which is about 50 per cent. of the weight of dry gelatin, this water is given up very slowly under reduced pressure of the water vapour. This shows that this last part is more firmly bound than the other. Further, the large amount of heat liberated in the earlier stages of swelling strongly indicates that a combination between gelatin and water takes place resulting in the formation of a hydrate or an adsorption complex. When the amount of water absorbed increases to about 20 per cent., the heat effect observed is small, though swelling still takes place.

It thus appears that the part of the water absorbed by gelatin in the earlier stages is more or less chemically bound, and is different from the rest of the water taken up inside the gel structure. The water taken up during the later part of the swelling process merely diffuses into the intermicellary space. As shown above, the light-scattering measurements provide us with a very good means of distinguishing between the two kinds of imbibition.

The *opalescence of gels during swelling* seems to be a very general phenomenon, and is met with in the case of several gels. Thus, pieces of agar when immersed in water behave in a manner very similar to that of gelatin. The author hopes to investigate further how the scattering of light in gelatin gels during swelling is affected by changing the temperature,  $H^+$  ion concentration, etc.

The above view of the author regarding the swelling of the individual micells is further supported by another interesting observation (Krishnamurti, *Nature*, 1929, 123, 242). A 2 per cent. gelatin gel at the isoelectric point is very turbid. When this is dried in a desiccator, at first there is no change in the gel, but after about a week it commences to clear up from the top. As the dehydration

proceeds, the whole gel becomes quite transparent by the time it shrinks to about two-thirds of its original volume. This observation seems to be quite significant, since it shows definitely that the removal of the liquid from the gel causes a shrinking of the micells and hence a very marked diminution in the light-scattering. In order to examine how far the above explanation of this phenomenon is correct, samples from the clear and opaque parts of the gel were examined in the cardioid ultramicroscope. It was found that the clear part was quite homogeneous, with only a few particles here and there. On the other hand, the middle part of the gel, which was in the process of clearing up, showed a multitude of extremely fine particles, just visible in the ultramicroscope; whereas the most opaque part, which is more or less the same as the original gel, showed innumerable particles which were distinctly bigger than those in the partially clear one. It is thus clear that the ultramicroscopic examination lends strong support to the above views regarding the shrinkage of the micells. These are probably loose molecular aggregates of gelatin enmeshing a part of the water in a loose state of combination. During the later part of the dehydration the loose water in the micells is removed, and this probably causes their shrinkage, and hence the loss of the turbidity of the gel. This view is further supported by another interesting observation made by the author, *viz.*, when a small dilute solution of hydrochloric acid is allowed to diffuse into a turbid 2 per cent. gelatin gel, the gel becomes clear, though it remains quite as rigid as before. The explanation of this effect probably is that the osmotic pressure exerted by the acid solution in the intermicellary liquid is strong enough to extract the water from within the micells. Further experiments are in progress to ascertain definitely the nature of the turbidity in gelatin gels at the isoelectric point.

Another point of interest with regard to the swelling of gels is that swelling, as ordinarily measured, increases enormously with rise of temperature. It is well known that the heat of swelling is positive, so that according to the principles of thermodynamics we should expect an increase of swelling with lowering of temperature, which is in contradiction to the observed facts. The difficulty of explaining this has also been pointed out by Wo. Ostwald (*Kolloid Z.*, 1928, **46**, 265). This difficulty, however, disappears if we distinguish between the two kinds of imbibition of the solvent as mentioned in this paper, *viz.*, (1) the first part which is bound in the gel micells by forces

which are probably chemical in nature, and which also causes the observed heat effects. (2) The part of the solvent which still continues to diffuse into the intermicellary space, causing no heat effects whatever.

During the initial part of the imbibition of water by gelatin there is a strong volume contraction. This has been carefully measured by Svedberg (*J. Amer. Chem. Soc.*, 1924, **46**, 2673) who found that this contraction increases with falling temperature. Rodewald found that the contraction during swelling is proportional to the heat effect, showing thereby that both are caused by the same factor, *viz.*, the interaction between gelatin and water. It therefore follows from the above that the heat of swelling and hence the amount of water bound in the gel should increase with lowering of temperature. Thus we see that what is apparently a contradiction is not really so, if we clearly examine the different factors in swelling. The curves of Arisz (*Koll. Chem. Beih.*, 1915, **7**, 49) giving the rate of swelling at different temperatures do not take the different factors in swelling into account. What he actually measured was the total swelling; and since the second part of imbibition, *viz.*, the diffusion of the solvent into the gel structure greatly preponderates in amount, it is natural to expect a net increase in swelling with rise of temperature, though the amount of water bound by the micells is lowered; for the process of diffusion is favoured by an increase in temperature.

Further investigations on the swelling of different gels are in progress.

#### *Summary.*

(1) A phenomenon observed by the author is described, *viz.*, that a piece of gelatin becomes opalescent as a result of swelling when immersed in water. To find out the exact significance of this observation, a 2 per cent. gelatin gel at  $p_H$  3 was allowed to dry until its concentration was about 20 per cent. and then the changes in the intensity of scattered light determined as this gel was allowed to swell in water. It was found that the Tyndall intensity increases at first and then diminishes as swelling proceeds.

(2) The following picture of the mechanism of swelling is put forward to explain the above results. During the earlier stages of swelling, we are concerned with an imbibition of the liquid, which is actually taken up inside the gel micells; and this causes an increase

in the volume of the micells and hence an increase in the light scattering capacity. The liquid which is still further taken up into the gel diffuses into the intermicellary space, thus causing a dilution of the gel and hence a diminution in its light-scattering capacity. Further, the opalescence observed when a dry piece of gelatin is immersed in water is probably also caused by the water penetrating into the gelatin piece and making the system heterogeneous.

(3) It has been shown how this view is in complete accord with the observations of other workers with regard to the heat of swelling, etc.

(4) Two other methods are being employed by the author to distinguish between the water which is more or less chemically bound in the gel, and the other which merely diffuses into the intermicellary space, viz., (a) by examining the Raman bands for water in gels of various concentrations, and (b) by examining the magnetic susceptibility of water in gels of various concentrations,  $p_H$  values, and at different temperatures.

(5) Another interesting observation of the author is described, viz., the clearing up of a turbid 2 per cent. gelatin gel during (a) its dehydration in a desiccator, and (b) the diffusion of dilute HCl into the gel. The significance of these observations with regard to the structure of micells is discussed.

(6) Since the heat of swelling is positive, according to the principles of thermodynamics, we should expect an increase of swelling with *lowering* of temperature; whereas actually swelling increases enormously with *rise* of temperature. This apparent difficulty has been overcome by distinguishing between the two kinds of imbibition, as suggested above. It has been shown that the amount of water bound in the gel increases with lowering of temperature, while the rest of the water, which diffuses into the intermicellary space, increases with rise of temperature.



## On the Mechanism of Coagulation of Colloids .

By SUBODH GOBINDA CHAUDHURY AND SATYAPRASAD  
ROYCHODHURY.

The two fundamental ideas, tacitly assumed by different investigators on the process of coagulation of a colloid were until recently :

(1) That equivalent amounts of the precipitating ions are necessary for coagulation of a colloid (Whitney and Ober, *Z. Phys. Chem.*, 1902, **39**, 633 ; *J. Amer. Chem. Soc.*, 1901, **23**, 842 ; Freundlich, *Z. Phys. Chem.*, 1910, **73**, 385 ; Freundlich and Schucht, *Z. Phys. Chem.*, 1913, **85**, 641 ; Freundlich and Zeh, *Z. Phys. Chem.*, 1924, **114**, 65 ; cf. also the views of Freundlich, Joachimson and Ellisch, *Z. Phys. Chem.*, 1929, **141**, 249 ; Weiser and Sherrick, *J. Phys. Chem.* 1920, **23**, 205 ; Weiser and Middleton: *J. Phys. Chem.*, 1920, **24**, 30 ; Dhar, Sen and Ghosh, *J. Phys. Chem.*, 1924, **28**, 457 ; Ghosh and Dhar, *Kolloid, Z.*, 1925, **36**, 189 ; 1926, **38**, 141 ; Dhar and Ghosh: *J. Phys. Chem.*, 1926, **30**, 628 ; Ghosh and Dhar: *J. Phys. Chem.* 1925, **29**, 435, 659),

(2) That the coagulation of a colloid in presence of an electrolyte takes place at critical potential mainly through the lowering of the charge of the particles by ions oppositely charged to that of the colloid [Powis, *J. Chem. Soc.*, 1916, **109**, 734 ; Freundlich and his co-workers (*loc. cit.*) and Dhar and his co-workers (*loc. cit.*) ; Kruyt and Willigen, *Z. Phys. Chem.*, 1927, **130**, 170 ; *Kolloid Z.*, 1928, **44**, 22 ; Ghosh, *J. Chem. Soc.*, 1929, 2693 ; Burton, *Phil. Mag.*, 1906, *vi*, **12**, 472 ; 1909, **17**, 583 ; cf. also the views of Mukherjee and Chaudhury, *J. Indian Chem. Soc.*, 1925, **2**, 296 ; Mukherjee, Chaudhury and Raichaudhury, *ibid.*, 1927, **4**, 493 ; Mukherjee, Raichaudhury and Bhattacharyya, *ibid.*, 1928, **5**, 735 ; Mukherjee, *Kolloid Z.*, 1929, **49**, 362].

Assumption (1) is based on assumption (2) and if they are true, it follows that the adsorbability and the coagulating power of a precipitating ion go hand in hand. That this is not true was first pointed

out by Ostwald (*Kolloid Z.*, 1920, **26**, 28) and afterwards experimentally shown by Sen (*Kolloid Z.*, 1926, **38**, 310) who observed that though sugar stabilises a  $\text{MnO}_2$  sol towards coagulation, the adsorption of copper ions instead of decreasing, increases in presence of sugar. One of us (Chaudhury, *J. Phys. Chem.*, 1928, **32**, 1481) has shown that adsorbability of an ion as measured analytically and its coagulating power do not show parallelism, and put forward a tentative suggestion that these results might be explained on the basis of a change in the dielectric constant and interfacial tension of the medium or the double layer surrounding each colloidal particle. Such a suggestion was primarily based on the conception of the mechanism of coagulation due to Mukherjee (Doctorate Thesis, London, 1921) and also on the views of Donnan (*Phil. Mag.*, 1901, **6**, 647) and Burton ("The physical properties of colloidal solutions," 1901, p. 203). Mukherjee and Chaudhury first (*loc. cit.*; see also Mukherjee, Chaudhury and Mukherjee, *J. Indian Chem. Soc.*, 1926, **3**, 349) pointed out the two-fold opposite effect of a non-electrolyte on the process of coagulation. Mukherjee (*loc. cit.*) suggested that the coagulation of a colloid in presence of an electrolyte depends on the value  $e^{-A/kT}$  where  $A$  is the work done by the colloidal particles before they can coalesce and  $T$  and  $k$  are the temperature and Boltzmann's constant respectively.

Now  $A$  evidently is equal to  $\frac{q^2}{Dd}$  where  $D$  is equal to the dielectric constant of the medium,  $q$ , the charge acquired by the particle after the addition of the electrolyte, and  $d$ , the distance between the centres of the colloidal particles at the point of their nearest approach.

So the term proportional to the rate of coagulation becomes

$$e^{-q^2/DdkT} \quad (\text{A})$$

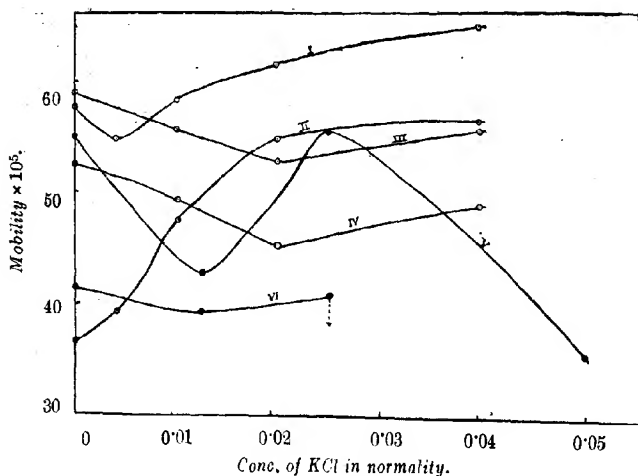
Now  $q$ , the charge acquired by a particle on the addition of an electrolyte depends also on the dielectric constant of the medium, since the number of bound ions (*cf.* Mukherjee, *Trans. Faraday Soc. loc. cit.*) will depend on the work term

$$W = \frac{n_1 n_2 e^2}{Dx} \quad (\text{B})$$

where  $n_1$  and  $n_2$  are the valencies of the primarily adsorbed and the bound ions,  $D$ , the dielectric constant and  $x$  the distance

between the ions at the point of their nearest approach, and  $e$  the electronic charge. It is clear that if by the addition of a non-electrolyte the dielectric constant decreases,  $W$  will increase with consequent diminution in  $q$ , the charge on the colloidal particles (*cf.* Mukherjee, *loc. cit.*). Therefore the value of the expression (A) will increase, but since (A) contains also  $D$ , a decrease in  $D$  will also decrease the value of (A). Thus the stabilising or sensitising effect of a non-electrolyte on a colloid towards precipitating electrolytes can be understood from the two-fold opposite effects of a change of dielectric constant mentioned above (*cf.* Mukherjee and Chaudhury, *loc. cit.*). From these considerations alone it is easy to see that the adsorbability and the coagulating power of a precipitating ion cannot go hand in hand. With the addition of a non-electrolyte interfacial forces are likely to change (*Cf.* Chaudhury, *loc. cit.*) and if the interfacial-tension-work, to be done before coagulation sets in, becomes low, necessarily the colloid will be stable even if the charge acquired by the colloidal particles is low, as interfacial forces are not sufficient to overcome the electrical repulsion though diminished. Recently Weiser (*J. Phys. Chem.*, 1930, **44**, 101) has criticised the above views because the interfacial force at the colloid-liquid interface is of a nonmeasurable or difficultly measurable magnitude. He prefers to explain the results on the basis of the change of di-electric constant alone. It is to be noted that the diminution of  $q$ , the charge on the colloidal particle takes place through a diminution in  $D$ , the di-electric constant of the double layer. It is, therefore, apparent that the same argument of explaining a factor in terms of a difficultly measurable or non-measurable quantity applies equally well also in the case of di-electric constant of the double layer and partially also in the case of the di-electric constant of the highly conducting mixtures of colloids, electrolytes and non-electrolytes. From the arguments given above it is also easy to see why a particular colloid is not characterised by a definite critical coagulation potential. Mukherjee and Chaudhury (*loc. cit.*) and Mukherjee, Raychaudhury and Rao (*J. Indian Chem. Soc.*, 1928, **5**, 697; *cf.* also Mukherjee, Chaudhury and Roychaudhury, *J. Indian Chem. Soc.*, 1927, **4**, 493) have shown that there is no such critical potential in the case of  $As_2S_3$  sol in presence of different mixtures of electrolytes and non-electrolytes (*cf.* curves I, II, III and IV taken from the paper by Mukherjee, Roychaudhury and Rao, *loc. cit.*).





Curves I and II refer to  $\text{As}_2\text{S}_3$  sol with 2½% and 10% MeOH respectively; curves III and IV refer to the same sol with 2½% and 10% EtOH; curves V and VI refer to copper ferrocyanide sol with 2½% and 10% cane sugar respectively.

One of us (S.G.C.) has found that copper ferrocyanide sol in presence of non-electrolytes also behaves similarly (cf. Curves V and VI; taken from an unpublished paper by Chaudhury shortly to be communicated for publication). Results similar in nature to the above have also been found with ferric hydroxide sol purely in presence of electrolytes by Mukherjee, Raychaudhury and Biswas (*J. Indian Chem. Soc.*, 1931, **8**, 373; cf. Kruyt and Willigen, *loc. cit.*; Kruyt and Briggs, *Proc. K. Akad. Wetensch. Amsterdam*, 1929, **32** 384; Briggs, *J. Phys. Chem.*, 1930, **34**, 1926; Weiser, *J. Phys. Chem.*, 1930, **44**, 101). Thus it can be stated that the coagulation of a colloid does not take place at a critical potential as postulated by Powis (*Z. Phys. Chem.*, 1915, **89**, 186), and Ellis (*ibid.*, 1912, **80**, 597) and therefore it is also not possible that there should be any parallelism between the adsorbability and coagulating power of an ion oppositely charged to that of the colloid.

The above view of the mechanism of coagulation furnishes also a ready explanation of the process of coagulation with simple electrolytes, mixtures of electrolytes and the phenomenon of acclimatization. Since the process of coagulation depends on the value  $e^{-q^2/DdkT}$  and since it has been found experimentally that colloids are coagulated with a relatively high concentration of electrolytes

with monovalent precipitating ions with a high cataphoretic velocity, it is to be noted that this is only possible through a great increase in  $D$  (partly through an increase in the interfacial tension). So in these cases coagulation takes place more through an increase in  $D$  than through a lowering in  $q$ . Low concentrations of electrolytes with bi- or trivalent precipitating ions are however required for coagulation of a particular sol. Bi- or trivalent precipitating ions lower the charge considerably (and this lowering is much more

augmented because the term  $\frac{-q^2}{eDkT}$  involves the square of  $q$ ) and therefore here coagulation takes place more through a lowering of  $q$  than through an increase in  $D$ . In this connection it is interesting to note the views of Burton ("Physical Properties of Colloidal solutions," 1921, p. 187) who states "The essential mechanism by which univalent ions cause coagulation *must be quite different* from that by which trivalent ions produce this result... Now if electrical conductivity is for any reason a potent factor in causing coagulation.....the influence of this factor might easily dominate the action with univalent ions but be of quite secondary importance in the case of trivalent ions." The picture of coagulation depicted above shows that this mechanism of coagulation by a univalent ion is *quite different* from that by a di- or trivalent ion.

Incidentally it will be well to mention here that Michaelis ("The effects of ions in colloidal systems," 1925, p. 67) advanced the view that coagulation of a colloid takes place due to the throwing back of the dissociation of the colloidal particle and in support of this he found that mastic sol at the coagulating concentration of hydrochloric acid does not absorb hydrogen ions. This fact was thought to be not in agreement with the physical theory of the double layer as apart from the chemical point of view held by Pauli and others (Pauli, *Kolloid Z.*, 1917, **21**, 49; 1921, **29**, 173, 281; 1924, **34**, 29, 145, 213; Usher, *Trans. Faraday. Soc.*, 1925-26, **21**, 406; Pennyquick, *J. Chem. Soc.*, 1930, 1447). From what we have stated above it will be sufficient to note that hydrochloric acid increases sufficiently the dielectric constant of the medium and thus brings about the coagulation of the mastic sol.

Coagulation with mixtures of electrolytes can also be explained on the basis of the views developed above as will be evident from the following tables:.

TABLE I.

The coagulating concentration of barium chloride in presence of increasing concentrations of sodium chloride with arsenious sulphide sol (*J. Indian Chem. Soc.*, 1924, **1**, 214).

% Conc. of NaCl.	% Conc. of BaCl <sub>2</sub> .	Sum.
0	100	100
20	134	154
50	115	165
66	80	146

Coagulating conc. of NaCl = 0.075 N = 100

Coagulating conc. of BaCl<sub>2</sub> = 0.00155 N = 100

TABLE II.

The cataphoretic velocity of arsenious sulphide sol with definite concentration of BaCl<sub>2</sub> in presence of increasing concentrations of NaCl (*J. Indian Chem. Soc.*, 1927, **4**, 493).

Conc. of BaCl <sub>2</sub> .	Conc. of NaCl.	Rate of migration × 10 <sup>5</sup> .
0	0	53.5
0.001 N	0	20.2
0.001	0.015 N	37.2
0.001	0.025	40.3
0.001	0.0375	39.7

From these results we see that the coagulating concentration of barium chloride at first increases and passing through a maximum again decreases. The cataphoretic velocity also shows a similar behaviour in presence of a constant concentration of barium chloride with increase in concentrations of sodium chloride. At first with increase in concentrations of sodium chloride the dielectric constant of the medium increases and also the density of electrical charge diminishes. Both these factors would tend to decrease the adsorbability of barium ions and therefore a higher concentration of barium ions would be necessary to increase the value of  $e^{-q^2/DdkT}$ . But with still higher concentrations of sodium chloride the density of electrical charge will increase (*cf. Mukherjee, Roychoudhury and Bhattacharyya, J. Indian Chem. Soc.*, 1928, **5**, 714, with this particular type of arsenious sulphide sol) so that the adsorbability of barium ion due to this factor will increase and eventually exceed the lowering in adsorbability of the same ion due to an increased dielectric constant; consequently

compared to lower concentrations of sodium chloride the coagulating concentrations of barium ions, *i. e.*, barium chloride will be diminished. It is needless to mention that the behaviour of a colloid towards mixtures of electrolytes will depend on the method of preparation of the sol and its initial electrolytic content, and each particular case should be considered individually on the basis of the charge of the colloid under these conditions.

The phenomenon of acclimatization can also be explained similarly. It must be mentioned that the  $p_H$  of the medium should not be changed with the addition of any single electrolyte, and therefore the considerations set forth above hold only for those electrolytes which do not affect the  $p_H$  of the medium appreciably.

It might be assumed that the above considerations are essentially the same as those of Kruyt and his collaborators (*loc. cit.*) who thought that the high dielectric constant with uni-uni-valent salts is responsible for the high cataphoretic speed; but it must be remembered that the dielectric constant should be abnormally high [*cf.* Mukherjee, Roychoudhury and Rao (*loc. cit.*)] in order to bring down the potential to a critical value; in the expression  $e^{-q^2/DdkT}$ , a small change in the value of  $D$  produces a great variation in the value of  $e^{-q^2/DdkT}$  and hence there is no reason to assume an abnormally high dielectric constant in order to explain coagulation at a high cataphoretic speed.



## Adsorption of Electrolytes by Activated Charcoal.

BY JNANENDRANATH MUKHERJEE, SATYAPRASAD ROYCHOU DHURY  
AND MONOMO HAN MAJUMDAR.

In recent papers Roychoudhury (*J. Indian Chem. Soc.*, 1931, 8, 433), Roychoudhury and Mukherjee (*Z. Phys. Chem.*, 1931, 157, 435) have dealt with experiments on the adsorption of acids and alkalis and hydrolytic adsorption in relation to Mukherjee's theory of the electrical double layer and have discussed the theories of Frumkin and Schilow in this connection. In his reply Frumkin (Frumkin, Burstein and Lewin, *Z. Phys. Chem.*, 1931, 157, 442) admits the adsorption of acids by hydrogen charcoal and states that this fact is beyond the scope of his theory, but he holds that it is not a contradiction of it. He argues that the ash contents of the charcoals have to be taken into consideration in explaining the adsorption by charcoal and admits that he has omitted considerations of the ash content in order to simplify matters. Frumkin and co-workers wonder as to the origin of hydroxyl ions in the electrical double layer whose exchange according to the postulates of Roychoudhury and Mukherjee (*loc. cit.*) gives rise to alkali on treating charcoal with neutral potassium chloride. In our papers it has been stated that charcoal adsorbs hydrogen ions from water (in the primary layer) and hydroxyl ions remain partly in the fixed and partly in the mobile sheets of the double layer. It is well known (Mukherjee and co-workers, *J. Chem. Soc.*, 1926, 3023; *J. Indian Chem. Soc.*, 1925, 2, 191) that chemically pure ignited silica acquires a negative charge in contact with water presumably through formation of silicate ions by interaction of the dioxide molecules on the surface with water and free hydrogen ions are present on the liquid side which are liberated as free acid in contact with neutral salt solution (*vide* also *Phil. Mag.*, 1922, 44, 321; *Kolloid Z.*, 1930, 52, 214). With reference to the present case Roychoudhury (*loc. cit.*) has shown that by continually washing negatively charged charcoals obtained from different sources with 'conductivity water,' the charcoal always acquires a positive charge. In the above adsorption experiments positively charged activated samples of sugar charcoal were used.

In the present paper the results of the following experiments with negatively charged activated sugar charcoal and the charcoal

which has, on continued washing with boiling water, a zero charge before becoming positively charged, are reported:

(1) Electro-osmotic experiments: (a) negatively charged sugar charcoal and sodium chloride, benzoic acid, caustic soda, hydrochloric acid and sulphuric acid; (b) electrically neutral charcoal and hydrochloric acid.

(2) Adsorption of (a) hydrochloric acid, sulphuric acid, sodium hydroxide and by negative charcoal (Sample A, Tables I, III); (b) sodium hydroxide, barium hydroxide, picric, sulphuric, and hydrochloric acids—measurements both by indicator and conductometric titration—by negative charcoal (Sample B, Tables V and VI) and by neutral charcoal (Sample C, Tables VII and VIII); (c) hydrochloric acid, barium and sodium hydroxide solutions by negative (Sample B) and neutral (Sample C) charcoal by conductometric titration (curves I to XV, Fig. 3—7).

(3) Hydrolytic adsorption of (a) sodium chloride and sodium benzoate by negative charcoal (Sample A, Table II); (b) sodium chloride by negative (Sample B) and neutral (Sample C, Table X) charcoals.

#### EXPERIMENTAL.

The preparation of the activated sugar charcoal (negative) was carried out in the manner described previously (Roychoudhury, *loc. cit.*). The temperature of activation was between 550° to 600°, and the time of activation was 6 hours. The charcoal was negatively charged in contact with conductivity water (electro-osmotic experiments). Two samples (A and B) were prepared.

The neutral charcoal (Sample C) was prepared as follows: About 100 g. of the charcoal prepared previously (but not activated) was boiled with 500 c.c. conductivity water for 15 minutes and the mixture was kept overnight. The sp. conductivity of the supernatant liquid was determined. The supernatant liquid was thrown off and the charcoal again boiled with 500 c.c. conductivity water for 15 min. The process was repeated about a dozen times. The final sp. conductivity of supernatant liquid recorded was  $4 \times 10^{-6}$  mhos at 22°. The charcoal was washed three times more with conductivity water but its sp. conductivity did not change any further. This sample of charcoal (16 times washed) was then activated in the manner as described previously (6 hours at 600°). The charge of this charcoal in contact with water was found electro-osmotically to be almost neutral.

*Measurement of Charge of Sugar Charcoal by  
Electro-osmotic Experiments.*

The electro-osmotic experiments were carried out as described in previous papers. The results are semi-quantitative. Ten gms. of charcoal were shaken with 100 c.c. solution and kept overnight. The charcoal was then introduced up to two fixed marks in the two limbs of the U-tube, and the whole tube including the side tube was filled with the solution. The electrodes were always connected with the mains (220 volts D.C.) and their relative positions were fixed. A small air bubble was introduced in the side tube by means of two three way stopcocks at the two sides of the U-tube. The movement of the air bubble for 3 minutes was noted twice in each direction (mean of four measurements). The agreement between the opposite movements was satisfactory. The measurements ( $29-30^{\circ}$ ) were reproducible to  $\pm 5$  per cent.

*Conductometric Titrations.*—The conductometric titration of the acid or alkali solution or of the supernatant liquid remaining after adsorption was carried out in an arrangement shown in the Figure 1. A wide-mouthed 100 c.c. Jena glass bottle was fitted with a rubber cork bored with four holes. These holes were used for admitting (1) the stem of a micro-burette, (2) two internally sealed glass tubes with two fused thick platinum electrodes maintained at a fixed distance apart suitable for measurements of the conductivity, (3) a stirrer and (4) a glass tube for passing pure hydrogen (to prevent the access of carbon dioxide during titration). The conductivity was measured by means of a Leeds Northrup conductivity bridge in an electrically controlled thermostat ( $35^{\circ} \pm 0.1^{\circ}$ ).

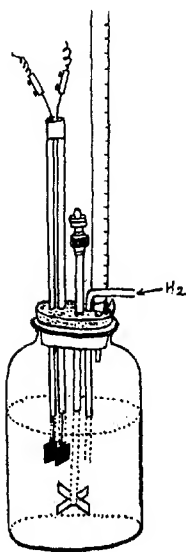


FIG. 1.

*Separation of the Intermicellary Solution from the Charcoal.*—The charcoal was at first separated from the solution by the help of a powerful centrifuge using borosilicate tubes.

The adsorption of carbon dioxide was later avoided in experiments with samples B and C by taking out supernatant liquid with a pipette after the particles have completely settled. The specific conductivity



of the alkaline solutions did not change by keeping them overnight in the Jena glass bottles. A slight change of specific conductivity was observed when the solution was kept in a centrifuging tube and rotated in the centrifuge. Time of contact was 24 hours in each case.

*Specific conductivity  $\times 10^3$  r.o. of the solution in different vessels.*

Electrolyte.	A measuring flask (freshly prepared solution).	100 c.c. Jena glass bottle.	100 c.c. Jena glass bottle (centrifuged solution).
0.002 N-NaOH	0.4946	0.4977	0.4665

*Preparation of Hydrogen* (Fig. 2).—The hydrogen was obtained from the electrolysis of caustic soda solution with platinum electrodes and freed from oxygen by passing the gas dried over sulphuric acid and calcium chloride through copper gauze heated electrically to about  $400^\circ$ . The gas was then passed through soda lime and bubblers containing respectively pure water and the solution to be used. The conductivity of the pure water was tested at intervals to ascertain the absence of electrolytic impurities in the gas.

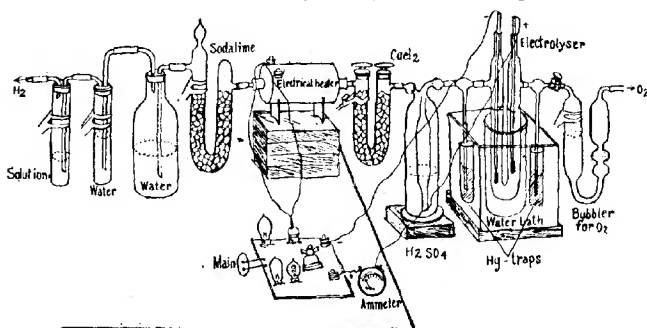


FIG. 2.

TABLE I.

0.5 G. charcoal (A); 50 c.c. solution; 24 hrs. contact;  
room temperature.

Electrolyte.	Normality from indicator titration		% Adsorption (approx.).
	Before.	After.	
HCl	0.0203	0.0186	8.3
	0.0101	0.009	10.4
	0.0407	0.0387	4.9
H <sub>2</sub> SO <sub>4</sub>	0.0203	0.0203	...
	0.0101	0.0101	...
	0.04	0.04	...
NaOH	0.0205	0.0205	...
	0.0108	0.010	...
	0.04	0.04	...
Benzoic acid	0.0203	0.0179	40
	0.0103	0.0080	22

TABLE II.

0.5 G. of charcoal (A); 50 c.c. solution; time of contact 24 hrs; room temperature.

Electrolyte.		pH values (Colorimetric Gillespie's Immersion Type)	
		Before.	After.
NaCl	0.02N	6.51	7.59
	0.01	6.59	7.18
	0.002	6.62	7.23
Na-benzoate	0.02N	7.63	8.22
	0.01	6.58	7.21
	0.002	6.58	6.81

TABLE III.

*Sulphuric Acid Solution.*

0.5 G. of charcoal (A); 50 c.c. solution; time of contact 24 hrs. room temperature.

Normality concentration.	pH by e.m.f. method		Sp. conductivity $\times 10^3$ in r. o.	
	Before.	After.	Before.	After.
0.1	1.21	1.21	26.1	26.1
0.02	1.74	1.73	6.40	6.38
0.01	2.08	2.07	3.52	3.57
0.002	...	...	0.829	0.777
0.001	...	...	0.419	0.396

TABLE IV.

*Electro-osmotic Experiments.*

10 G. of charcoal (A); 100 c.c. solution; time of contact 24 hrs; room temperature. Rate of flow in cms/3 min.

Conc. in normality.	NaCl.	Benzoic acid.	NaOH.	HCl.	H <sub>2</sub> SO <sub>4</sub> .
0	-0.4*	-0.4	-0.4	-0.4	-0.4
0.0002	-0.81	-1.09	-1.8	-1.5	-1.4
0.001	-4.65	-1.4	-10**	...	...
0.002	-6.9	-1.35	...	...	...

\* Minus indicates negative charge.

\*\* Electrolysis took place.

TABLE V.

1 G. of charcoal (B); 100 c.c. solution; time of contact 24 hrs; temperature 35°.

Electrolytes.		Sp. conductivity $\times 10^3$ in r. o.		% Adsorption (approx.).
		Before.	After.	
NaOH	0.002N	0.481	0.322	33
"	0.01	3.24	2.91	10
Ba(OH) <sub>2</sub>	0.0033	0.869	0.530	39
Picric acid	0.002	0.788	0.446	43
H <sub>2</sub> SO <sub>4</sub>	0.002	0.837	0.754	10
"	0.01	3.61	3.39	6
HCl	0.002	0.914	0.586	36
"	0.01	5.81	5.06	13

TABLE VI.

1 G. of charcoal (B); 100 c.c. solution; time of contact 24 hrs; room temperature.

Electrolytes.		Normality (indicator titration)		% Adsorption (approx.).
		Before.	After.	
NaOH		0.002	0.00145	27
"		0.0100	0.00916	9
Ba(OH) <sub>2</sub>		0.0033	0.0021	37
H <sub>2</sub> SO <sub>4</sub>		0.0020	0.00185	6
"		0.001	0.000976	2
"		0.02	0.0197	slight
HCl		0.002	0.00143	27
"		0.01	0.00891	10
"		0.02	0.0188	slight

TABLE VII.

1 G. of charcoal (C); 100 c.c. solution; time of contact 24 hours; temperature 35°.

Electrolytes.		Sp. conductivity $\times 10^3$ in r. o.		% Adsorption (approx.).
		Before.	After.	
NaOH	0.002 N	0.481	0.420	13
"	0.01	3.24	3.10	4
Ba(OH) <sub>2</sub>	0.0033	0.869	0.763	12
Picric acid	0.002	0.788	0.661	16
H <sub>2</sub> SO <sub>4</sub>	0.002	0.837	0.780	7
"	0.01	3.61	3.48	3.6
HCl	0.002	0.914	0.583	36
	0.01	5.81	4.97	14

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TABLE VIII.

1 G. of charcoal (C); 100 c.c. solution; time of contact 24 hrs; room temperature.

Electrolytes.	Normality (indicator titration)		% Adsorption (approx.)
	Before.	After.	
NaOH	0.002	0.00198	...
"	0.01	0.0099	...
Ba(OH) <sub>2</sub>	0.0033	0.0030	10
H <sub>2</sub> SO <sub>4</sub>	0.002	0.00194	2
"	0.01	0.00993	...
"	0.02	0.0197	...
HCl	0.002	0.00143	27
"	0.01	0.00801	10
"	0.02	0.0188	...

TABLE IX.

*Electro-osmotic Experiments.*

Rate of flow in cms./3 min.

	C.	B.
Water	nil	—0.4 (as with A)
0.0002 N-HCl	nil	No measurement was taken.
0.002 N-HCl	—0.4	Ditto

TABLE X.

Adsorption of 0.002 N-NaCl by active sugar charcoal. 1 G. Charcoal; 100 c.c. solution; time of contact 24 hrs.; temp. 35°.

Sample.	p <sup>H</sup> (by e.m. f. method)	
	Before.	After.
B	6.3	7.54
C	6.3	7.51

*Determination of Adsorption of Acids and Alkalis by Activated Charcoal (B and C) as determined by Conductometric Titration (Fig. 1).*

Conductometric titrations were carried out to determine the adsorption of Ba(OH)<sub>2</sub>, HCl, and NaOH by both negatively charged and zero charged activated sugar charcoal (B and C). 1 G. charcoal was treated in each case with 100 c.c. solution at room temperature,

time of contact being 24 hours. 50 c.c. of solution was used in each titration.

(a) Fig. 3—curve I represents the titration of approximately 0.0033N-Ba(OH)<sub>2</sub> while curves II and III of the same baryta solution after contact respectively with samples B and C by 0.1 N-HCl. (b) Fig. 4—curve IV, the titration of 0.002 N-HCl; curves V and VI of the same hydrochloric acid solution after contact respectively with samples B and C by baryta solution. (c) Fig. 5—curve VII, the titration of 0.01N-HCl; curves VIII and IX of the same hydrochloric acid solution after contact respectively with samples B and C by baryta. (d) Fig. 6—curve X the titration of approximately 0.002N-NaOH, curves XI and XII of the same caustic soda solution after contact respectively with samples B and C by 0.1N-HCl. (e) Fig. 7—curve XIII, the titration of approximately 0.01N-NaOH; curves XIV and XV of the same solution after contact respectively with samples B and C by 0.1N-HCl. The amounts of adsorption as estimated from the conductometric titration curves are given in the following table:

TABLE XI.

Sample of charcoal	Electrolytes.	Concentration in normality		% Adsorbed (approx.).
		Initial.	Final.	
B	Ba(OH) <sub>2</sub>	0.0032	0.00172	46
„	HCl	0.01	0.0088	12
„	HCl	0.002	0.0013	35
„	NaOH	0.0085	0.00756	11
„	NaOH	0.0017	0.00128	25
C	Ba(OH) <sub>2</sub>	0.0032	0.00252	21
„	HCl	0.01	0.0088	12
„	HCl	0.002	0.0013	35
„	NaOH	0.0085	0.0085	...
„	NaOH	0.0017	0.0017	...

The comparison of the amounts of adsorption of different electrolytes by the samples of charcoal (B and C) in different procedures of measurement is given in the following table:

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TABLE XII.

*Comparison of Adsorption.*

Normality of electrolytes and samples.	% Adsorption (approximately by different methods)		
	Specific conductivities.	Titration.	Conductometric titration.
0.002 NaOH (B)	33	27	25
„ (C)	13	nil	nil
0.01 „ (B)	10	9	11
„ (C)	4	nil	nil
0.0033 Ba(OH) <sub>2</sub> (B)	39	37	46
„ (C)	12	10	21
0.01 HCl (B)	13	10	12
„ (C)	14	10	12
0.002 „ (B)	36	27	35
„ (C)	36	27	35

FIG. 3.

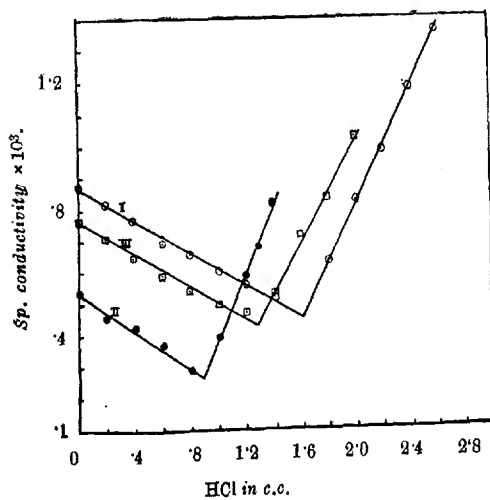


FIG. 4.

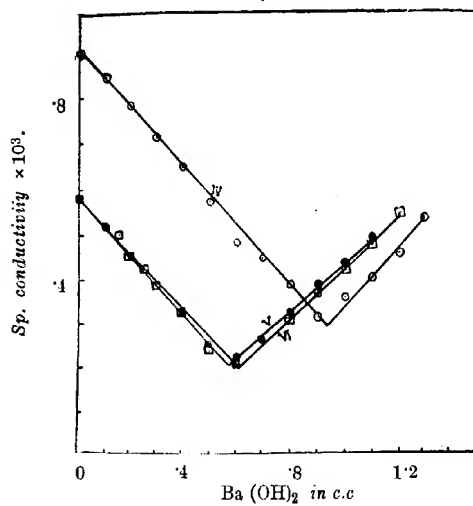


FIG. 5.

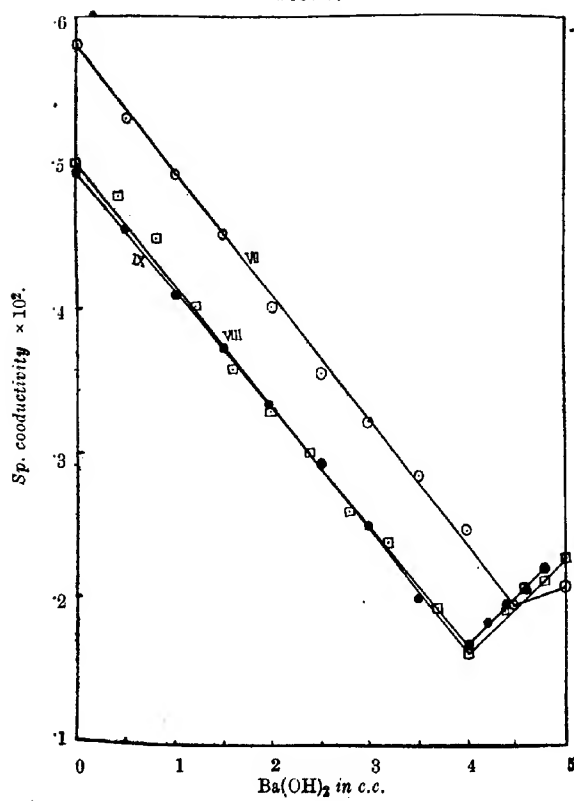


FIG. 6.

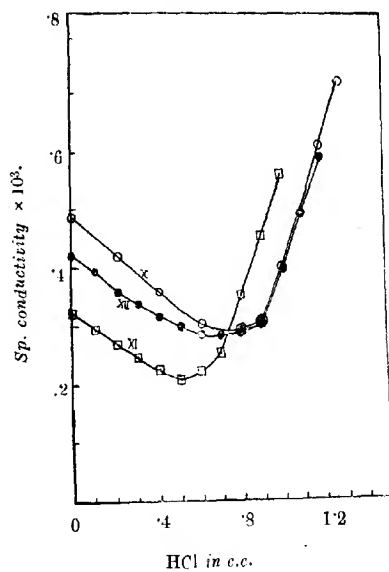
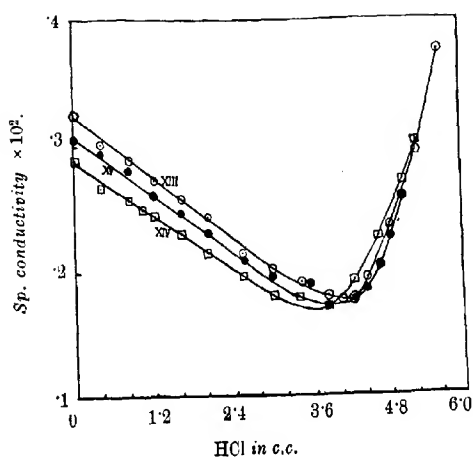


FIG. 7.





*Adsorption of Acids and Alkalis by Charcoal and the Electric Charge of the Charcoal Surface.*

The main point in Frumkin's theory is that activated charcoal, unless it is freed from oxygen, *e.g.*, by hydrogenation in presence of platinum, behaves as an oxygen electrode. As a result of the large surface, the oxygen or hydroxyl ions that tend to pass into the solution and which impart to the surface a positive charge, are present in ponderable amounts. Anions and neutral salts can displace the hydroxyl ions, and this explains the observed alkalinity of neutral salts, *e.g.*, sodium chloride. No reference is made to the specific behaviour of the anions regarding their capacity to displace the hydroxyl ions. Such oxygen charcoal (positively charged) would thus adsorb acid, and a 'carbo' salt would be formed at the surface.

The theory is based on the classical electrochemical theory of solution tension, and hence the nature of the anion should be of no moment so long as the hydrogen ion activity is the same. It ignores the presence of substances other than carbon in the interface. Frumkin does not measure the electrical charge of the charcoal surface, and assumes it to be such as would fit in with the theory. On the other hand, according to the views formulated by us, the adsorption of ions is assumed to be at the root of these reactions, and is determined by the nature of the surface, that is, by the inter-atomic arrangement of the various atoms present on the surface, as also on the arrangement of the molecules or groups formed by interaction of these atoms and of the loose atoms that may be present.

Adsorption of neutral molecules and possibilities of chemical interaction are kept in view, but the part played by the distribution of ions in the double layer and the interchange of ions between the double layer and the solution and their relation to the electrical charge of the surface is separately investigated, as in such cases they play an indisputable rôle. This point of view has also the merit of correlating these reactions with the vast mass of observations on the properties of electrically charged colloids, the adsorption of ions and associated phenomena. In the previous papers evidence has been given indicating the presence of both cations and anions on the surface. It has been shown that on washing, electrolytic impurities come out of the charcoal surface, with the consequent change from negative to a positive charge of the

surface. It is desirable to ascertain how far the removal of these impurities changes the adsorptive properties of charcoal. For this purpose the acid and alkali adsorption by samples B and C have been compared. So far in work with activated charcoal, indicator titration has been used to determine the amount of adsorption of acid or alkali. It is possible that weak cations and anions are exchanged. In such a case indicator titration alone will fail to indicate their presence. Accordingly, the amount adsorbed was ascertained also from the diminution of the specific conductivity and by conductometric titration of the clear, supernatant liquid remaining after adsorption. The slope of the conductometric titration curve shows that weak anions or cations are not present in the liquid after adsorption. There is in some cases a difference in the amount adsorbed as determined from the specific conductivity, indicator titration and conductometric determinations. We are inclined to ascribe this to greater accuracy of the conductometric titrations. The difference between the amounts adsorbed shown by the change in the conductivity and the conductometric titration in some cases, may in part be the result of the approximate interpolation used in connection with the latter but it requires closer examination.

*One definite result emerges from these experiments, namely that on washing, the adsorption of alkali definitely diminishes, but that of hydrochloric acid remains unchanged. (vide Tables V, VI, VII and VIII). This is to be related to the fact that the charge of the surface changes from negative to neutral, showing that acidic impurities are removed, and that these are responsible for the greater adsorption of the alkali.*

The strong adsorption of hydrochloric acid by both negative and neutral charcoal is interesting. It cannot be accounted for by Frumkin's theory, neither does it indicate molecular adsorption of hydrochloric acid as would appear from the sequel. It would seem possible that the carbinol groups or oxide linkages are responsible for the adsorption of hydrochloric acid as a result of the reaction of the type which gives rise to chlorhydrins (Sen and Barat, *J. Indian Chem. Soc.*, 1927, **4**, 22; also Brönsted, Kilpatrick and Kilpatrick, *J. Amer. Chem. Soc.*, 1929, **51**, 428), but Table IV shows that chlorine ions are strongly adsorbed as such. We are, therefore, inclined to refer the strong adsorption of hydrochloric acid to the primary adsorption of chlorine ions.

The net charge of the surface will, of course, be determined by the excess of ions of one sign that is adsorbed. In this connection it should be remembered that the charcoal surface has a strong affinity for the hydrogen ions and consequently the negative charge does not increase strongly in presence of the acid as it would do otherwise.

Another interesting point is the greater adsorption of barium hydroxide. There is the possibility that the different preparations of charcoal would show specific differences. The greater adsorption of barium hydroxide shows again a need for considering the specific adsorption of each ion. Table I also illustrates both these points. Sample A, prepared in the same manner, shows that sodium hydroxide is not adsorbed at all. It should be pointed out, however, that the adsorption has been determined by indicator titration only, which we find gives smaller adsorption than that deduced from conductometric measurements.

Sulphuric acid is adsorbed very slightly, if at all, while benzoic acid is also slightly adsorbed. The great difference between the adsorption of hydrochloric and sulphuric acids again shows that the hydrogen ion activity is not the moot point in determining acid adsorption, a result which definitely contradicts Frumkin's theory.

Table III illustrates (see also curves I to XV) the reliability of the conductometric measurements used for determining adsorption. At higher concentrations of the acid, the amount adsorbed being small, it is difficult to observe an appreciable change in the conductivity.

A few words should be added on the electro-osmotic effects of hydrochloric and sulphuric acids on negative charcoal (sample A, *vide* Table IV). The two acids give almost the same effect. Unfortunately the data could not be extended to higher concentrations as the amount of charcoal ran short. The agreement shows that we are dealing with the net effect and that the greater adsorption of chlorine ions is partially neutralised by the adsorption of hydrogen ions.

The marked effect of sodium hydroxide on the electric charge is interesting in view of the weak adsorption noted. It should be stated, however, that in Table I the adsorption of alkali was measured by titration, which we found to give low results. Sample A was prepared in the same manner as sample B, and from Tables V and VI it will be found that the sample B adsorbed alkali considerably. The greater effect of the alkali on the charge is to be associated with

the weaker adsorption of sodium ions. The results however, do not show to what extent cations or anions of strong bases or acids are displaced from the surface.

*Summary.*

1. Activated sugar charcoal which is initially negatively charged, acquires zero charge by simply washing with conductivity water, before it ultimately acquires a positive charge.

2. Adsorptions of acids and alkalis by both negative and neutral charcoals have been compared by the method of indicator titration as also from the diminution of the specific conductivity and by conductometric titration of the clear supernatant liquid remaining after adsorption.

3. The slopes of the conductometric titration curves show that weak anions or cations are not present in the liquid after adsorption.

4. It is found that the adsorption of alkali is definitely less in the case of neutral charcoal than in the case of negative charcoal. The adsorption of hydrochloric acid is however the same in both cases.

5. Hydrochloric acid is strongly, while sulphuric acid is very slightly adsorbed by both negative and neutral charcoals.

6. Hydrochloric and sulphuric acids have been found to have almost the same electro-osmotic effects on negative charcoal. Also sodium hydroxide possesses a marked electro-osmotic effect on negative charcoal.



## On Some Technical Aspects of Gaseous Explosions.

By HEMENDRA KUMAR SEN.

The problem of gaseous explosions is daily assuming greater and greater importance with the enormous increase of the automotive requirements of the world on the one hand, and the significance which explosions in general have for the coal mines. In the former, gaseous explosions have to be controlled so as to give a most suitable impetus to the piston of an engine cylinder, whereas in the latter, explosions have to be entirely prevented. Although the two objectives are different, investigations are fundamentally dependent on the same principle, namely that of studying the chemical and the physical nature of explosion. By the brilliant researches of Mallard, Le Chatelier, Berthelot in France, Dixon, Wheeler, Rhead, Payman, McDavid, Bone, Ellis, Garner, Coward, Mason, David and others of the English school, and Nernst, Haber, Bjerrum, Holborn, Hemming Pier, Budda, von Wartenberg, Wohl, Siegel, Jorissen, Burmeister and others in the continent of Europe, the science of explosion has been greatly advanced. Limits of explosive composition, their ignition temperatures and the temperatures produced by the explosion of these mixtures and their propagation are, in fact, shortly the scope of these investigators. The fruits of the fundamental researches in the laboratories in this direction, though not as adequate as expected, must, however, continue to be the guiding principle in achieving greater efficiencies in engine explosions or greater safety in the mines.

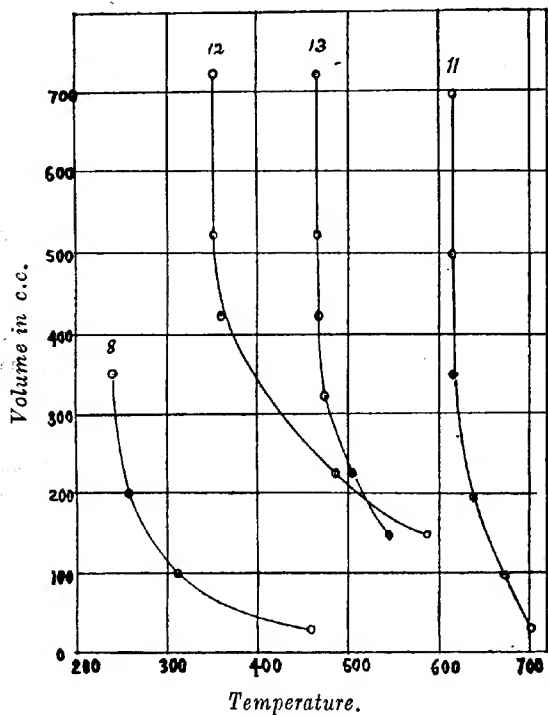
From the ordinary values of ignition temperatures of explosive mixtures, one is apt to under-rate the danger that actually exists even working with gases at temperatures which are commonly known to be considerably lower than their ignition temperatures, found by any of the methods that are usually employed. Commonly, there are four methods of ignition temperature determination viz., (1) by enclosing or passing the gas mixture into a heated vessel, (2) by direct contact with a hot surface at any point of the inflammable mixture, (3) igniting by adiabatic compression, and (4) by an electric spark.

It may be observed that in (2) and (4) instantaneous ignition is mostly aimed at and secured, and as such, these distinguish themselves from the other two methods where the influence of "time-lag" is more conspicuously present. The reason of this under-rating of danger lies in not appreciating the influence of "time-lag" or pre-flame period in an explosion. By this is meant that even if a particular temperature be regarded as the ignition point of an explosive mixture, by maintaining the same explosive mixture at a somewhat lower temperature for a somewhat longer period, one could initiate explosion. The explanation is that although the ignition point indicates a temperature at which the chemical action is capable of propagating itself with the violence of explosion, it does not mean that at somewhat lower temperatures no appreciable chemical reaction takes place. If, therefore, at a somewhat lower temperature a gas is maintained in an insulated condition, any the least chemical reaction would continue to add heat to the system, and, ultimately by the increase of temperature, so accelerate the reaction that an explosion is possible. This period before the explosion actually takes place is the "pre-flame" period. Where no explosive violence is noticed in the beginning, chemical reaction may proceed and ultimately, depending upon the degree of insulation, an explosion may take place. Theoretically, if a mixture of hydrogen and oxygen were enclosed in a perfectly heat-insulated vessel, and if we assumed that even at  $0^{\circ}$  or at temperatures considerably lower than  $0^{\circ}$  a chemical reaction between hydrogen and oxygen takes place, then, with the lapse of time, the heat of reaction accumulating may assume such a dimension that an explosion in many hundreds of years may take place. In practical explosions, therefore, to know the ignition temperature is not enough; in minimising such explosions, the determination of what may be termed the lowest ignition temperature is of fundamental interest. It is evident that the term "lowest ignition temperature" is inaccurate unless one defines the pre-flame condition, both with regard to insulation and temperature. It is, further, obvious that it is well nigh impossible to define accurately the pre-flame condition. Hence in our experiments we have taken the lowest ignition temperature of a gas as that temperature at which it explodes without sensible "time-lag." In order to have reproducible results, it is clear that a rigidity of standard is essential, otherwise the ignition temperatures would scarcely be reproducible in value.

The source of ignition and the method of effecting the same are of very great importance in explosions. Adiabatic explosions have no direct reference to mine explosions, but relate only to engine explosions which we shall discuss later. In mine explosions, ignition by contact with flames, hot surface or sparking forms in many cases the source. But more often one can imagine that contact with hot surface or flame can be the immediate cause of explosions in mines. If that is so, experiments on the determination of ignition temperatures of gases by bringing a hot surface in direct contact with gases would form a more suitable basis for studying safety limits. In 1917, McDavid (*J. Chem. Soc.*, 1917, 111, 1003) made some preliminary determinations of the ignition points of gases by enclosing them in soap bubbles and bringing them in contact with hot surfaces assuming that the pre-flame period was not present in such explosions as the ignition was instantaneous. The results that he obtained were not naturally reproducible, because he neither regulated the exact size of bubbles, nor did he control within a reasonable degree of uniformity the state of the room in which he carried out his experiments. Besides, his method of determining the temperature of the hot surface electrically left somewhat to be desired from the point of precision, although, to his great credit, it must be said that he instituted a very important method in the study of ignition temperatures. In 1927, the study of the ignition temperatures of gases enclosed in soap bubbles was undertaken in order to investigate the cause of explosion in a confectionary shop in Calcutta, where apparently, from local inspection, no direct cause of explosion could be found. It was noticed that if the size of the soap bubbles and the condition of draught in the room and the temperature of the bubbles were kept constant, a hot source in the shape of a platinum spiral heated by an electrical current, could ignite these bubbles at the same temperature, the experimental error scarcely exceeding  $\pm 0.5$  per cent. Encouraged by this reproducibility, we designed a special apparatus for producing increasingly larger bubbles, and it was noticed, as will be evident from the curves below, that above 500 c.c. volume, the soap bubbles ignited practically at the same temperature although from smaller sizes up to about 500 c.c. there was a fall in the ignition temperature. But comparing the values obtained in these experiments with those of other observers under separate conditions of experiment, one is impressed with the fact that under altered conditions, the lowest ignition



temperatures of inflammable gases are not infrequently two to three hundred degrees lower than are usually supposed to be. A perceptible lag is noticed in the experiments with larger bubbles. This may be compared to the stationary stage of explosion (Hinshelwood, *Proc. Roy. Soc.*, 1929, **A122**, 610). In ordinary language one could say that the catalytic reaction initiated in the pre-flame period, being exothermic (the curves refer to oxy-hydrogen explosion, Mitra, Chatterjee and Sen, *J. Indian Chem. Soc.*, 1932, **9**, 167) affords sufficient heat to accelerate the chemical reaction to the stage of explosion, the large size of the bubble imparting



to it a more insulated condition and hence a lowered ignition temperature. An alternative explanation, both as regards the constancy of ignition temperature as also its lowering, under these conditions may be found in the reduced thickness of the soap film with increase in the size of the bubbles. As large bubbles would mean virtually the non-existence of any dividing septum between the gas volume and the source of ignition, a uniform ignition temperature is to be expected. This does not explain the remarkably low temperature

of ignition, for which we have to depend upon the pre-flame period or the generally insulated nature of the soap bubbles when they are large. In fact, to these conditions must be added also the catalytic behaviour of the wires themselves.

The next point of technical importance in ignition temperature determinations is to find out a composition of the inflammable mixture which would stand higher compression ratios when used as the working substance in internal combustion engines, without pre-ignition. We have accordingly examined the effect of dilution on ignition temperatures of gases by the soap bubble method, and, as expected, on diluting the inflammable gas mixture with inert gases like nitrogen or carbon dioxide, a substantial increase in the ignition temperature takes place. It is well known that the highest efficiency in gas engines is not attained by the use of the strongest mixture but a somewhat weaker mixture, due mainly to the fact that a greater rise of temperature, and therefore of pressure, in excess of the proportion of the fuel used, is obtained when exploding the weaker than when exploding the strong mixture. In a strong mixture containing say, 11·4% coal gas in coal gas—air mixture *in the engine*, the temperature rise after explosion was 1700°, whilst in the case of a weak mixture (8·8% coal gas in coal gas air—mixture *in the same engine*) the temperature was 1430°. The ratio between the two temperatures is 1·19, but the corresponding amounts of heat supplied by the fuel are in the ratio of 1·3. In the first case, the ideal thermal efficiency was found by Prof. Hopkinson in a 40 B.H.P. Crossley gas engine (*Proc. Inst. Mech. Eng.*, April, 1908) to be 39·4%, whereas with the weaker mixture, 42·4%. The pressure falls rather more rapidly in the adiabatic expansion of the weaker mixture, but the difference in this respect is not very material, the work done in the gas engine cycle being mainly determined by the rise of pressure which occurs on explosion due to the temperature. The determination of the maximum temperature of an explosion flame is, therefore, of very great practical importance in giving an approximate indication without actual experiment, which of the inflammable mixtures would be suitable for attaining the highest efficiency in the same internal combustion engine. A graphical method for easily calculating the temperatures of flames produced from different compositions of inflammable mixtures was developed by the author (*Proceedings of the Indian Science Congress*, 1926, p. 153; Sen, "High Temperature Flames and their Thermodynamics, 1931, p. 81

cf. also Goodenough and Felbeck, *Bull. Engineering Exp. Station*, 1924, No. 139, published by the University of Illinois, Urbana), the usefulness of which in this direction is obvious.

When a fuel burns, the thermal energy that is liberated raises the temperature of the products of combustion to an extent depending upon the specific heats of the latter. As the temperature rises the products of combustion, however, begin to dissociate. This dissociation derives the necessary thermal energy from the fuel itself and in consequence, the temperature of the flame is lower than what would have been the case, had there been no dissociation. Besides, with increased temperature, the specific heat varies also considerably, a correct value of which is necessary for the calculation of flame temperature. In my calculations originally in 1926 I used Langen's values for the mean molecular heats of gases at different temperatures and at constant pressure:

$$\text{CO}_2 = 8.7 + 0.0026t$$

$$\text{H}_2\text{O} = 7.9 + 0.00215t$$

$$\text{Permanent gases} = 6.8 + 0.0006t.$$

I have since recalculated the temperatures of some of the more important flames from Bjerrum's data as summarised by him for mean molecular heat capacities of gases at high temperatures. Above 2714° for  $\text{CO}_2$  and 3064° for steam, and 2367° for the permanent gases, I have extrapolated, and as such, the results are obviously less accurate.

Let us now for simplicity assume that we are burning pure carbon and let  $H_1(T)$  represent the quantity of heat absorbed by the dissociation of  $\text{CO}_2$  at the temperature  $T$ ,  $X$  being the fraction dissociated. Then,

$$H_1(T) = qX \quad \dots (1)$$

where  $q$  represents the heat of formation of  $\text{CO}_2$  from  $\text{CO}$  and  $\text{O}$ . Further let  $H_2(T)$  be the heat utilised in raising the temperature of  $\text{CO}_2$ ,  $\text{CO}$  and  $\text{O}$  to  $T$  degrees absolute. This quantity is equal to  $Q - H_1(T)$ , where  $Q$  represents the heat of formation of  $\text{CO}_2$  from  $\text{C}$ . Then,

$$H_2(T) = Q - H_1(T) = T \left\{ (1-X) \cdot S_{\text{CO}_2} + X \cdot S_{\text{CO}} + \frac{X}{2} \cdot S_{\text{O}_2} \right\} \dots (2)$$

where  $S$  represents the specific heats of gases at the temperature  $T$ . For the combustion of hydrogen into water, the same notations with

$H_1$  may be employed using appropriate values for  $q$ ,  $X$ , and  $Q$ . Now, in order to find the value of  $T$ , the equation (2) will have to be solved graphically. This would give the temperature of a carbon flame. The interpretation of the equation is that there must be found a temperature at which the fraction dissociated,  $X$ , and the specific heats have such values that the relation

$$Q - qX - T \left\{ (1-X) \cdot S_{CO_2} + X \cdot S_{CO} + \frac{X}{2} \cdot S_{O_2} \right\} = 0 = Y \dots (3)$$

is valid. In other words, if the temperature and the first member of equation (3) be represented by abscissa and ordinate respectively, then the point at which the curve intersects the temperature line will be the solution of the equation, because at this point alone the value of that expression is equal to zero.

In arriving at the value of  $X$  (the fraction dissociated of  $CO_2$  or  $H_2O$  at different temperatures) use has been made of the fundamental equation,  $\frac{d \ln K}{dT} = \frac{U}{RT^2}$  in an integrated form, the thermodynamically indeterminate integration constant,  $i$ , being taken from Haber's data. Thus,

$$\log K = \frac{29580}{T} - 2.44 \log T + 0.00074 T - 2.609 \text{ for } CO_2 \dots (A)$$

$$\log K = \frac{25029}{T} - 3 \log T + 0.00055 T + 3.333 \text{ for } H_2O \dots (B)$$

where  $K$  stands for the dissociation constant at the temperature  $T$ . As the dissociation of  $CO_2$  may be represented by



$$K, \text{ the equilibrium constant} = \frac{X^3}{X^3 - 3X + 2} \dots (4)$$

We can now tabulate two sets of data: one, the values of  $K$  at different temperatures directly from the equation (A), or (B), and another, the values of  $K$  with different values of  $X$  from the equation (4), whence it is obvious, the relation between  $X$  and  $T$  may be found out. Having now obtained the values for  $X$  at different temperatures we can solve the equation (3) graphically as described above. It is also evident that by combining the equations for carbon-oxygen and

hydrogen-oxygen flames, and neglecting the water gas reaction for the sake of simplicity, the temperature of a hydrocarbon flames may be likewise calculated. Here the equation will have the form

$$Q - qX - T \left\{ (1-X) \cdot S_{\text{CO}_2} + X \cdot S_{\text{CO}} \frac{+X}{2} \cdot S_{\text{O}_2} \right\} +$$

$$Q' - q'X' - T \left\{ (1-X') \cdot S_{\text{H}_2\text{O}} + X' \cdot S_{\text{H}_2} + \frac{X'}{2} \cdot S_{\text{O}_2} \right\} = 0 = Y.$$

Below is a table of calculated flame temperatures by this method of graphical solution which has been found useful in many instances.

	From Langen's Sp. heat data.	From Bjerrum's Sp. heat data.
Hydrogen burnt with requisite quantity of oxygen	...	3360T
Carbon burnt with requisite quantity of oxygen	3540 T	3505T
Carbon burnt with requisite quantity of air	2320 T	2210 T
Carbon burnt with 10% excess of air, the whole of the air being pre-heated to 1000°	2684 T	...
Carbon burnt with requisite quantity of air, the whole of it being pre-heated to 1000°	...	2687 T
Carbon burnt with 50% excess of air, the whole of it being pre-heated to 1000°	2465 T	...
Carbon monoxide burnt to CO <sub>2</sub> with the requisite quantity of oxygen	...	2970 T
Carbon monoxide burnt to CO <sub>2</sub> with requisite quantity of air pre-heated to 1000°	...	2725 T
Hydrocarbon (C=84%, H=14%, S=2%) burnt with requisite quantity of air	...	2187 T
Do, air being pre-heated to 1000°	2760 T	
Producer gas (H=8%, CH=4%, CO=28%) with requisite quantity of air	...	2682 T
Do, both air and gas being pre-heated to 1000°	2350 T	1900 T
		2180 T

The values so obtained are in some cases in fairly close agreement with those obtained experimentally by some of the workers, and reveal the effect of pre-heating and excess of secondary air very strikingly. The decidedly higher temperature of a hydrocarbon flame than that of producer gas would according to emission law diminish the heat periods of a furnace, but how this will affect the knock properties of inflammable mixtures is not yet clear. These are problems which are of fundamental interest in the technology of internal combustion engines.

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## The Dependence of Quantum Efficiency on the Frequency of Effective Monochromatic Radiation in Photochemical Reactions.

By J. C. GHOSH AND R. M. PURKAYASTHA.

In a previous paper (*J. Indian Chem. Soc.*, 1929, 6, 827), on the photochemical reduction of ferric salts by mandelic, lactic and tartaric acids, it has been shown that in these reactions whose temperature coefficient of reaction velocity is almost unity, a marked increase in quantum efficiency occurred with increase in frequency of exciting radiation. Table I gives a summary of results obtained.

TABLE I.

Reductant.	Mols of ferric chloride reduced per quantum of absorbed radiation of wave-length		
	488 $\mu$ .	448 $\mu$ .	390 $\mu$ .
Mandelic acid	1	1.18	1.36
Tartaric acid	0.49	0.52	0.8
Lactic acid	0.42	0.52	0.8

Monochromatic radiation was obtained in this case from a mercury lamp with the aid of suitable filters.

This increase in the quantum efficiency with increase in frequency was also observed in all cases where bromine is used as the photo-active reagent. Results of a preliminary investigation have been already published (*Z. Phys. Chem.*, 1930, 9, 128; *J. Indian Chem. Soc.*, 1927, 4, 409). In these investigations however, strictly monochromatic radiation could not be obtained, as even with the aid of very well-devised filters, small intensities of light from the different parts of the spectrum could not altogether be excluded. The reaction vessels hitherto used, were made of quartz plates cemented together. Reproducible results in photochemical reaction with bromine are difficult to obtain in presence of even very slight impurities and hence it was considered desirable to exclude the use of cement in the construction of reaction vessels. In the present paper an account of the improvements in the technique of experiments carried out with these objects in view, and some preliminary experimental data are recorded.



*Experimental Arrangement.*

Light from a quartz mercury lamp run from a constant voltage of 220, at 3 amperes, was focussed on the slit of a D 41 Hilger quartz monochromator by a quartz condenser F. 278. The monochromator was placed inside a wooden box blackened inside, the collimator arm carrying the slit only projecting out of the box. In front of the slit in the telescope, a metal shutter fitting the recess of the monochromator can be raised or lowered from outside the box with the aid of a string and pulley. A thick brass attachment to the telescope arm, carried a quartz lens beyond the shutter, and the reaction vessel, on which light from the slit was made to fall in an approximately parallel beam by means of this lens. The same brass attachment also carried a Moll-microthermopile with a second shutter in between the reaction vessel and the thermopile. The second shutter is also operated in the same way as the first one.

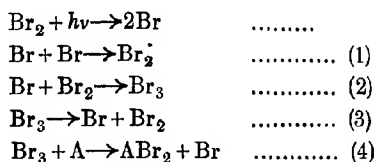
*Construction of the reaction vessel.*—A quartz tube, 1 cm. in length, external diameter 1 cm., internal diameter 6 mm., was ground optically flat at both ends. Optically flat circular plates of fused quartz were placed at both ends of this quartz tube, the whole mounted in a thick brass tube and the quartz end plates pressed tight by means of brass screw caps. For surfaces which are perfectly flat, it has been found that water did not escape perceptibly in six hours, and carbon tetrachloride in an hour. The reaction vessel was completely filled with the reacting solution, and after exposure to light taken out of its brass case, placed inside solution of potassium iodide, the end-plates pulled apart and the liberated iodine titrated with a 0.01N-thiosulphate solution delivered from a micro-burette.

*Measurement of absorbed radiation.*—The intensity of absorbed radiation was measured by means of a Moll thermo-relay system. The sensitiveness of the system was determined by means of a standard carbon filament lamp which had been calibrated by the Bureau of Standards, Washington. It was found that 100 ergs. per square cm. per second incident on the thermopile produced a galvanometer deflection of 56 mm.

The intensity of absorbed radiation was found by observing the deflections produced by the monochromatic radiation (1) after passing through the solvent alone, and (2) after passing through the reacting solution.

*Experimental Results.*

A. *Photobromination of cinnamic acid in solutions of carbon tetrachloride.*—In this case it has been found that only those radiations which are absorbed by free bromine, are photochemically active. The velocity of reaction can be deduced from the following equations (*Z. Phys. Chem.*, 1930, **9B**, 165.)



Hence

$$\begin{aligned} -\frac{d[\text{Br}_2]}{dt} &= K_2[\text{Br}_2] \sqrt{\frac{I}{Nh\nu}} \cdot \sqrt{\frac{1}{K_1}} \cdot \frac{K_4 A}{K_3 K_4 A} \\ &= K_5[\text{Br}_2] \sqrt{\frac{I}{Nh\nu}}, \end{aligned}$$

where  $K_1, K_2, K_3, K_4$  are the velocity constants of the dark reactions 1, 2, 3, 4 and A is the concentration of cinnamic acid. This equation has been verified for blue light (mean wave-length  $488\mu\mu$ ) with respect to the intensity of absorbed radiation and concentration of cinnamic acid which were varied within wide limits (*J. Indian Chem. Soc.*, 1927, **4**, 409). The velocity of reactions were measured when exposed to radiations of the following wave-lengths: 546, 436, 366,  $313\mu\mu$ ; the experimental data are recorded in Table II.

Cinnamic acid does not absorb radiations 546, 436 and  $366\mu\mu$  while very dilute solutions of it 1 cm. thick completely absorb radiations  $313\mu\mu$ . On the other hand bromine strongly absorbs radiations 546, 436 and  $366\mu\mu$ , while for radiations  $313\mu\mu$ , bromine, dissolved in carbon tetrachloride, has a very weak absorption.

It will be seen from the table that photobromination takes place very rapidly on exposure to radiations 546, 436 and  $366\mu\mu$ , while radiations  $313\mu\mu$  even though of higher frequency and completely absorbed by cinnamic acid is ineffective. This observation is in itself a convincing proof of the hypothesis that the primary photochemical reaction is the decomposition of bromine molecules by radiations which they absorb followed by subsequent dark reaction chains.

TABLE II.

Cinnamic acid—0.047*M* ; Br<sub>2</sub>—0.0205*M* ; Temp. 24°.

$t_1$ in secs.	$t_2$ in secs.	$(a-x_1)$ .	$(a-x_2)$ .	$2.3 \frac{1}{t_1-t_2} \log \frac{a-x_1}{a-x_2}$ .	$I$ in ergs per sq. cm.	$\sqrt{\frac{I}{N h \gamma}}$ .	$2.3 \frac{1}{t_2-t_1} \log \frac{a-x_1}{a-x_2} = k_3$ .
45 $\mu$	300	1320	0.01862	0.014	$2.79 \times 10^{-4}$	$315.6$	28
435 $\mu$	360	1200	0.01869	0.01373	$3.666 \times 10^{-4}$	232	40
366 $\mu$	300	1200	0.01890	0.01445	$2.978 \times 10^{-4}$	94	55.5
313 $\mu$	300	2000	0.0205	0.0200	no reaction	74*	...

\* The absorption due to bromine is negligible, the entire light energy being absorbed by cinnamic acid.

It will also be noticed that

$$K_5 = \frac{\frac{2.3}{t_2 - t_1} \log \frac{a - x_1}{a - x_2}}{\sqrt{I/Nh\nu}}$$

$$= \frac{K_2}{\sqrt{K_1}} \cdot \frac{K_4 A}{K_3 + K_4 A}$$

which has already in previous papers been shown to have a constant value for the same frequency of radiation, increases considerably as the frequency of active radiation increases. For the concentration of cinnamic acid (0.047M) used in these experiments, the factor

$$\frac{K_4 A}{K_3 + K_4 A}$$

is practically unity, hence the increment in  $K_5$  with increasing frequency is due to increase in the value of  $K_2/\sqrt{K_1}$ . If we consider collisions with the molecules of the solvent carbon tetrachloride to be always elastic, then



is possible only when the kinetic energy of the bromine atoms + the energy of the reaction - the kinetic energy of the resultant bromine molecule corresponds to a possible transition between the internal energy levels of the bromine molecule. Similar considerations apply to the reaction



It appears that the value of  $K_2$  increases with increment in the internal energy of the bromine atom; the same is also true of  $K_1$  the factor  $K_2/\sqrt{K_1}$  however increasing with increase in the frequency of absorbed radiation.

B. *The photochemical reaction between bromine and organic hydroxy acids in presence of  $\text{Br}^-$  ion in aqueous solutions.*—It has already been shown that for this reaction only the light that is absorbed by free bromine and not by the  $\text{Br}_3$  ion is effective (*J. Indian Chem. Soc.*, 1929, 6, 361). This conclusion is further supported by investigation of the action of radiation of frequency  $313\mu$ . The extinction coefficient of an aqueous solution

of bromine for this radiation is about 100, whereas the extinction coefficient due to  $\text{Br}_3^-$  ion is immeasurably large. The fraction of radiant energy absorbed by free bromine is thus negligible compared with that absorbed by  $\text{Br}_3^-$  ion, and we accordingly find that photo-bromination does not take place with measurable velocity when the system is exposed to radiations  $313\mu$ .

In this reaction, the concentration of bromine atom per c.c. in the stationary state is given by

$$\sqrt{\frac{I}{Nh\nu} \cdot \frac{1}{K_1}} \quad \dots \quad \dots \quad \dots \quad (1)$$

where  $I$  is the value of light energy per sq. cm. per sec. absorbed by free bromine in a solution of 1 cm. thickness, and  $K_1$  is the velocity of combination of bromine atoms to form molecular bromine.

The number of reaction nuclei formed per second is

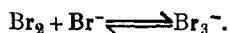
$$K_2 \sqrt{\frac{I}{Nh\nu} \cdot \frac{1}{K_1}} [A^-] \quad \dots \quad \dots \quad (2)$$

where  $[A^-]$  is the concentration of the anion of hydroxy acid. The activation of a free bromine molecule by collision with a hot molecule resulting from reaction between a bromine atom and the anion of organic acid is responsible for the production of a reaction chain whose length 'L' is given by

$$L = \frac{K_a[\text{Br}_2 \text{ free}] + K_b[\text{Br}_3^-]}{K_b[\text{Br}_3^-]}$$

on the assumption that collision with a  $\text{Br}_3^-$  ion often breaks the chain. But

$$[\text{Br}_2 \text{ free}] = \frac{0.07[\text{Br}_3^-]}{[\text{Br}^-]} \text{ due to equilibrium}$$



or

$$L = \frac{\frac{0.07K_a}{[\text{Br}^-]} + K_b}{K_b} = \left[ \frac{K_3}{[\text{Br}^-]} + 1 \right].$$

$$\text{Hence } \frac{d[\text{Br}_2]}{dt} = \frac{K_2}{\sqrt{K_1}} \cdot \sqrt{\frac{I}{Nh\nu}} \cdot [A^-] \left[ \frac{K_3}{\text{Br}^-} + 1 \right]$$

$$= K_5 \sqrt{\frac{I}{Nh\nu}} \text{ for constant value of } A'.$$

The velocity of reaction is zero molecular with respect to bromine which has been actually found to be the case.

TABLE III.

Mandelic acid—273M; Br<sub>2</sub>—0·01343M; KBr—0·1515M (Br<sup>−</sup>—0·1166M; free Br<sub>2</sub>—0·00504M; Br<sub>3</sub><sup>−</sup>—0·0084M; Temp. 22°.

$Nh\nu$ .	$\epsilon_{\text{Br}_2}$	$\frac{I_t}{\epsilon_{\text{Br}_2}}$ in ergs.	$\frac{I_f}{\epsilon_{\text{Br}_2}}$ in ergs.	$\sqrt{\frac{I_f}{Nh\nu}}$	$x/t^*$	$\frac{x/t}{\sqrt{\frac{I_f}{Nh\nu}}}$
545 $\mu$	$219 \cdot 7 \times 10^{10}$	0·18	60 46·2	$0 \cdot 453 \times 10^{-5}$	$3 \cdot 93 \times 10^{-8}$	$8 \cdot 6 \times 10^{-3}$
435 $\mu$	$275 \cdot 7 \times 10^{10}$	1·8	194·3 48·6	$0 \cdot 42 \times 10^{-5}$	$13 \cdot 15 \times 10^{-8}$	$31 \cdot 3 \times 10^{-3}$
366 $\mu$	$327 \cdot 5 \times 10^{10}$	5·8	86·5 8·1	$0 \cdot 157 \times 10^{-5}$	$7 \cdot 25 \times 10^{-8}$	$46 \cdot 2 \times 10^{-3}$

With lactic acid the values of  $x/t / \sqrt{\frac{I_f}{Nh\nu}}$  are  $25 \cdot 8 \times 10^{-3}$

and  $32 \times 10^{-3}$  for 435 $\mu$  and 366 $\mu$  respectively. The concentration of all the substances is the same as in the case of mandelic acid.

In the above table  $I_t$  is the total light absorbed per sq. cm. by the reaction mixture and  $I_f$  is the fraction of light absorbed by free bromine molecules only. This quantity has been obtained in the following way

$$I_f = I_t \frac{[\text{free bromine}]}{[\text{free bromine}] + [\text{Br}_3^-] \epsilon_{\text{Br}_3} / \epsilon_{\text{Br}_2}}$$

The ratio  $\epsilon_{\text{Br}_3} / \epsilon_{\text{Br}_2}$  was obtained from the extinction coefficient measurements of Br<sub>3</sub> and Br<sub>2</sub> (*J. Indian Chem. Soc.*, 1929, 6, 361).

\*  $x/t$  is the change in the concentration of bromine per c.c. per sec. due to the photochemical reaction, i.e., total reaction—dark reaction. Unlike the case of bromination of cinnamic acid, the dark reaction is not negligible here.

For  $366\mu$  the ratio was determined with the present arrangement consisting of a monochromator and thermopile and found to be nearly 5.8.  $x/t$  is the number of mols transformed per c.c. per sec.

In a previous paper (*Z. Phys. Chem.*, 1930, **9B**, 285) it has been shown that for the same frequency of radiation, the zero-molecular velocity constant is proportional to the square-root of the intensity of absorbed radiation. Hence the increase in the value of  $K_5$  with the increase in the value of  $\nu$  is due to increment of the factor

$$\frac{K_2}{\sqrt{K_1}} \cdot \left[ \frac{K_3}{\text{Br}^-} + 1 \right].$$

We might consider that  $K_2$  does not change with frequency of absorbed radiation for every collision of a bromine atom with a molecule of organic acid may be expected to result in chemical change. The value of  $\sqrt{K_1}$  increases with increment in the value of the quantum absorbed, as has been stated in the previous section.

Therefore the chain length  $\left[ \frac{K_3}{\text{Br}^-} + 1 \right]$  must increase very considerably with increase in  $\nu$  and this is to be expected, for the larger the energy of the hot molecule resulting from reaction between a bromine atom and the anion of organic acid the greater is the probability of its starting a reaction chain, and increasing its length.

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## Optische Untersuchungen an Uranverbindungen.

VON FRITZ EPHRAIM.

Das Absorptionsspektrum zahlreicher Uranverbindungen zeigt insofern eine Ähnlichkeit mit demjenigen der seltenen Erden, als es durch eine Anzahl schmaler, nahezu linienartiger Banden ausgezeichnet ist. Das Auftreten dieser Banden war bei den seltenen Erden mit der defekten Natur des N-Niveaus der Elektronen in Zusammenhang gebracht worden (Ephraim, *Ber.*, 1926, 59, 2692) und wenn nun beim Uran ähnliche Erscheinungen sich wiederholen, so liegt die Vermutung nahe, dass auch dieses Element eine ausbaufähige, innere Elektronenschale enthält. Infolge der periodischen Natur des Systems der Elemente darf die Erwartung ausgesprochen werden, dass in angemessener Entfernung von den seltenen Erden die Erscheinung der Neuauuffüllung einer scheinbar abgeschlossenen Elektronenschale sich wiederholt. Wenn angenommen wird, dass es wieder die drittausserste Elektronenschale ist, die diese Ergänzung erfährt, so darf vermutet werden, dass die drei äussersten Elektronenschalen der drei letzten Elemente Thorium, Protaktinium und Uran den folgenden Bau besitzen:

	O	P	Q
Th	2 6 10 —	2 6 2	2
Pa	2 6 10 1	2 6 2	2
U	2 6 10 2	2 6 2	2

Es würde also der "Lanthanidengruppe" eine "Thoridengruppe" entsprechen. Dass dies bisher nicht deutlicher wurde, mag damit zusammenhängen, dass die Gruppe bereits beim dritten Glied abgeschnitten ist, das Zweite Glied wegen seiner Seltenheit nicht zur ausführlichen Untersuchung gekommen ist, und dass die chemische Ähnlichkeit der einzelnen Glieder, die in einer solcher Gruppe in Erscheinung treten sollte, in den ersten Gliedern noch nicht völlig bemerkbar ist, wie ja zum Beispiel das Ce r lange ohne Anstand



wegen seiner Vierwertigkeit im periodischen System in einer anderen Senkrechten untergebracht wurde, wie das Lanthan.

Wenn nun die Ursachen der linienartigen Struktur des Uranspektrums ähnliche sind, wie die der Spektren der seltenen Erden, so sollten auch die *Veränderungen*, die das Spektrum der Uransalze mit wechselndem Anion erfährt, den gleichen Regeln unterliegen, die für die Erdspektren gefunden wurden (Ephraim, R. Bloch und P. Rây, *Ber.*, 1926, **59**, 2692 ; 1928, **61**, 65, 72, 80 ; 1929, **62**, 1509, 1520, 1639). Hier hatte sich gezeigt, dass das Spektrum mit zunehmender Polarisationswirkung des Säurerestes zunehmend nach dem violetten Ende verschoben wird. Betrachtet man zum Beispiel die Spektren der Halogenverbindungen, so ist hier die Ladung der Säurereste stets die gleiche, die anziehende Wirkung aber und somit die auf das Metallatom ausgeübte Polarisation steigt vom Jod zum Fluor, weil dieses letztere am kleinsten ist, also sein Mittelpunkt, in dem die Ladung konzentriert gedacht werden kann, dem Metallatom am nächsten gelagert ist.

Die Prüfung dieser Verhältnisse beim Uran zeigte nun in der Tat, dass auch hier häufig eine Verschiebung der Spektrallage nach Violett stattfindet, je stärker polarisierend der Säurerest wirkt. Die Nachprüfung ist hier aber stark erschwert, weil die Spektren sich vielfach nicht unter Bewahrung aller Linien verschieben, sondern mehr in ihrer Gesamtheit und unter Konservierung einiger Hauptlinien. Schon ältere Untersuchungen, zum Beispiel diejenigen von Nichols und Howes (*Publ. of the Carnegie Inst. Washington*, 1919) geben für den Vergleich ein recht brauchbares Material. Trotz der sehr grossen Zahl von Untersuchungen über das Uranspektrum liegen jedoch genügend exakte Zahlen bisher nur für Verbindungen des *sechswertigen* Urans, speziell Uranylverbindungen, vor. Es konnte nun nachgewiesen werden, dass die Sachlage bei anderen Wertigkeitsstufen, speziell der vier- und dreiwertigen, ganz die gleiche ist. Leider musste das Material etwas lückenhaft bleiben, da nicht alle gewünschten Verbindungen dieser Klasse hell genug sind um gute Absorptionsspektren zu geben, und da sie zum Teil auch schwierig in genügender Reinheit darstellbar sind. Doch ist das untersuchte Material reichlich genug, um keinen Zweifel an der Richtigkeit der Vermutung zu lassen.

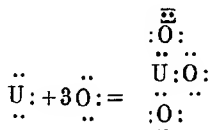
In einer Beziehung ist nun das Uran für die Nachprüfung der Theorie den seltenen Erden noch überlegen, nämlich darin, dass mit Leichtigkeit verschiedene *Wertigkeitsstufen* untersuchbar sind.

Auch bei den seltenen Erden treten ausser der Dreiwertigkeit andere Stufen auf, aber vierwertiges Cer zeigt kein linienartiges Absorptionsspektrum und die wenigen bekannten zweiwertigen Verbindungen sind meist so dunkel gefärbt, dass Absorptionsbezirke überhaupt nicht erkennbar werden. Der Arbeitshypothese nach sollte das Spektrum der Uranverbindungen um so weiter nach Rot liegen, je niedriger die Valenzstufe ist. Denn um so weniger Elektronen hat das Uranatom an seinen negativen Verbindungspartner bei der Salzbildung abgegeben. Je stärker sich der Atomrumpf nach Abgabe der Valenzelektronen zusammengezogen hat, um so mehr Energie ist nötig, die Elektronenverschiebung, die dem Absorptionsspektrum zugrunde liegt, in ihm vorzunehmen. In der Tat ist die einzige bekannte Verbindung des sechswertigen Urans, die nur Halogen enthält, das Uranhexafluorid,  $\text{UF}_6$ , völlig farblos, (A. v. Trasse, *Z. anorg. Chem.*, 1932, **204**, 184) besitzt also ihre Absorption, wenn überhaupt, höchstens im Ultraviolett. Die Uranylverbindungen sind zwar gefärbt, doch liegt ihr Spektrum, wie die Tafel zeigt, sehr wesentlich weiter zum Violett hin, wie das der niederwertigen Verbindungen. Das Spektrum des *Uranpentachlorides* zeigt dann die erwartete Rotverschiebung; aus diesem Spektrum ist übrigens ersichtlich, dass das Pentachlorid nicht etwa nur eine lockere Additionsverbindung von Hexachlorid und Tetrachlorid ist, denn das *Tetrachlorid-Spektrum* ist völlig verschieden. Es zeigt seinerseits gegenüber dem Pentachlorid ebenfalls eine beträchtliche Rotverschiebung. Wenn auch einige schwache Linien nur wenig gegenüber den kurzwelligsten Pentachloridlinien nach Rotverschoben sind, so liegt doch derjenige Teil des Spektrum, der nach Masse und Wirkung der ausschlaggebende ist, sehr deutlich nach dem langwelligen Ende hin. Nicht ganz spruchreif ist die Sachlage bei den Spektren der *dreiwertigen* Verbindungen. Der allgemeine Eindruck ist zwar der einer weiteren Rotverschiebung, aber sie ist mässig und für die energetische Veränderung, die zu erwarten ist, zu gering. Ich glaube aber vermuten zu dürfen, dass dies nur eine Folge unserer unzureichenden Apparatur ist. Der benutzte Spektrograph gestattete keine Aufnahmen von Wellen, die länger als  $670\mu$  sind und es darf angenommen werden, dass Absorptionen mit grösserer Wellenlänge im Spektrum noch vorhanden sind. Die älteren Untersuchungen von Zimmermann, (*Annalen*, 1882, **213**, 300) die leider quantitativ kaum auswertbar sind, sprechen durchaus dafür.

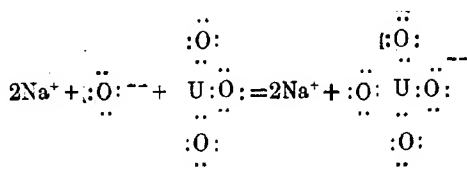
Die Verschiebungen bei Doppelsalzbildung, bei Hydratisation sowie bei Lösungsbildung waren im allgemeinen gleicher Art, wie bei den seltenen Erden beobachtet.

Für das Auftreten des linienartigen Spektrums bei Uranverbindungen ist es demnach gleichgültig, in welcher Oxydationsstufe dies Element vorliegt, jedoch scheint es erforderlich zu sein, dass das Uranatom Elektronen abgegeben hat. Ist es kovalent, hat es also keinen Elektronenverlust erlitten, oder hat es gar, wie in Uratanen, Elektronen aufgenommen, so findet sich kein Linien-spektrum. Die Verbindungen können zwar gefärbt sein, zeigen aber nur breite Bandenspektren.

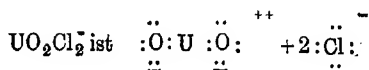
Farblos ist zum Beispiel das sechswertige Fluorid,  $\text{UF}_6$ , das keinesfalls eine polare Verbindung ist, sondern zu den, "umhüllten" Verbindungen gehört. Ohne linienhafte Absorption ist ferner das Trioxyd,  $\text{UO}_3$ , das, ähnlich dem Schwefeltrioxyd, ebenfalls als kovalente Verbindung zu deuten ist, die durch Zusammentritt der Atome ohne Abgabe von Elektronen entstanden ist:



Gleiches gilt natürlich für das Peroxyd,  $\text{UO}_4$ . Auch die Uranate zeigen nur bandenartige, nicht linienartige Absorption, da in ihnen nicht nur keine Abspaltung, sondern im Gegenteil eine Anlagerung von Elektronen an das Uranatom stattgefunden hat:



Ganz anders ist die Sachlage bei den Uranylverbindungen. In diesen stark dissociierenden Salzen hat das Uranatom Elektronen an das Chloratom abgetreten und es ist dadurch die Vorbedingung für die Entstehung des linienartigen Spektrums geschaffen:

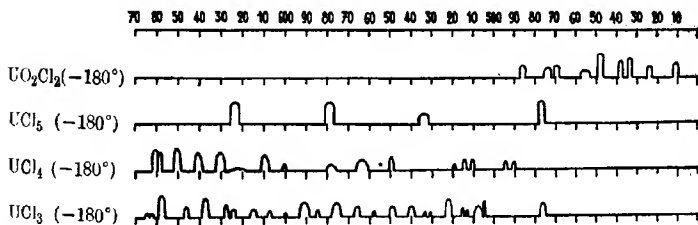


Das Gleiche ist natürlich der Fall in den Verbindungen des niederwertigen Urans des vier- und dreiwertigen wo dieses Element als ausgesprochenes Metall auftritt, also gegen den Säurerest Elektronen verloren hat.

Die Uranylverbindungen zeigen bekanntlich auch schöne linienartige Fluoreszenzspektren. Diese unterliegen den gleichen verschiebungsgesetzen, wie die linienartigen Absorptionsspektren, wie bereits aus den alten Messungen von Nichols und Howes herausgelesen werden kann.

Aus dem ziemlich umfangreichen Versuchsmaterial, das später an anderer Stelle ausführlich veröffentlicht werden wird, sein nur zwei Beispiele hier etwas näher erörtert, die die Sachlage in ihrer Komplikation zeigen. Das eine ist der Vergleich der verschiedenen Wertigkeitsstufen bei den Chloriden (Tafel I.), für den die

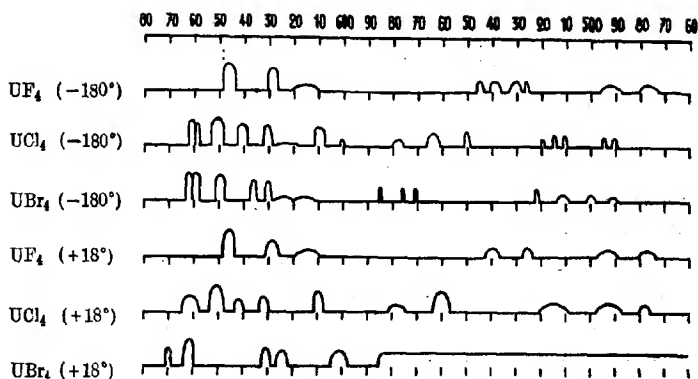
TAFEL I.



Wiedergabe der Kurvenbilder und des Zahlenmaterials genügen mögen, da eine kurze Discussion bereits oben stattgefunden hat. Die erwartete Verschiebung ist genügend ersichtlich zumal wenn berücksichtigt wird, dass das farblose  $\text{UCl}_6$  ein Linienspektrum im sichtbaren Teil nicht mehr besitzt und dass die Apparatur eine weitere Beobachtung des  $\text{UCl}_3$ -Spektrums nach Rot hin nicht erlaubte.

Das andere Beispiel ist das Bild der Spektren vom Fluorid, Chlorid und Bromid des vierwertigen Urans bei Zimmertemperatur und bei  $-108^\circ$  (Tafel II). Aus den Spektren bei Zimmertemperatur

TAFEL II.



ersieht man, wie sehr im Gegensatz zu den Verbindungen der seltenen Erden das Spektrum vom Säurerest abhängig ist. Ein direkter Vergleich zwischen Chlorid und Bromidspektrum ist kaum möglich. Es hängt dies sicherlich damit zusammen, dass die beiden Verbindungen ein *verschiedenartiges Atomgitter* besitzen. Da ist es nun sehr lehrreich, wenn man sieht, wie nach Abkühlung auf  $-180^\circ$  sich das Spektrum des Chlorides nur insofern verändert, als breitere Banden in einzelne Linien aufgespalten werden, auch einige neue Linien auftreten, während das Spektrum des Bromides eine vollständige Umwandlung erfährt. Es ist nun dem Chloridspektrum durchaus ähnlich geworden, die Lagerung der Atome im Kristall ist offenbar verändert und die Gitterstruktur beider Halogenide nunmehr identisch. Die Rotverschiebung des Bromides gegenüber dem Chlorid ist aber jetzt, wenn überhaupt vorhanden, so nur unbedeutend. Was das Fluorid anbetrifft, so liegt dessen Spektrum gegenüber dem der anderen Halogenide deutlich nach Violett. Es ändert bei der Abkühlung seine Modifikation nicht, dieselbe ist aber offenbar nicht direkt mit der des Chlorids vergleichbar, denn die Linien zeigen eine ziemlich abweichende Gruppierung.

Sehr schön und durchaus der Theorie entsprechend sind die Verschiebungen bei den Spektren der *Uranyl-Doppelsalze*. Bezüglich dieser muss aber auf die spätere Veröffentlichung verwiesen werden.

Den Kurventafeln liegen die folgenden Messungsdaten zugrunde: Die in Klammern geschlossenen Zahlen bedeuten die Intensitäten der Linien (geschätzt).

*Uranylchlorid*, wasserfrei ( $\text{UO}_2\text{Cl}_2$ ). 485-486 $\mu$  (5); 472 $\cdot$ 5-475 $\mu$  (4); 468 $\cdot$ 5-470 $\mu$  (5); 453-457 $\mu$  (3); 447 $\cdot$ 1-448 $\cdot$ 8 $\mu$  (10); 437 $\cdot$ 6-438 $\cdot$ 6 $\mu$  (7); 433-434 $\cdot$ 2 $\mu$  (8); 423-424 $\cdot$ 5 $\mu$  (?) 5; 410-411 $\cdot$ 7 $\mu$  (?) 6.

*Uranpentachlorid*, ( $\text{UCl}_5$ ). 622-625 $\mu$  (9); 577 $\cdot$ 5-580 $\cdot$ 5 $\mu$  (9); 532-536 $\mu$  (4); 476-478 $\mu$  (10).

*Urantetrachlorid* ( $\text{UCl}_4$ ). 660-661 $\cdot$ 5 $\mu$  (9); 658-659 $\mu$  (8); 648 $\cdot$ 5-652 $\cdot$ 5 $\mu$  (10); 639-642 $\mu$  (8); 629-632 $\mu$  (8); 623-626 $\mu$  (1); 619-622 $\mu$  (1); 608-611 $\mu$  (7); 600-601 $\mu$  (3); 576-580 $\mu$  (8); 561-566 $\mu$  (5); 549-550 $\cdot$ 5 $\mu$  (6); 510-511 $\mu$  (5); 519-519 $\cdot$ 5 $\mu$  (3); 514-515 $\mu$  (5); 494-495 $\mu$  (4); 490-491 $\mu$  (4).

*Urantrichlorid*, ( $\text{UCl}_3$ ). 664-665 $\mu$  (2); 662-663 $\mu$  (2); 656-659 $\mu$  (10); 645 $\cdot$ 5-647 $\mu$  (5); 636-638 $\cdot$ 5 $\mu$  (9); 627-628 $\mu$  (4); 624-625 $\mu$  (4); 614-616 $\mu$  (4); 607-608 $\mu$  (3); 600 $\cdot$ C $\mu$  (2); 589-593 $\mu$  (7); 584 $\cdot$ 5-585 $\mu$  (3); 574-578 $\mu$  (7); 565-567 $\mu$  (5); 558 $\mu$  (2); 548-550 $\mu$  (5); 539-541 $\mu$  (5); 533 $\cdot$ 5 $\mu$  (2); 531 $\mu$  (1); 521-523 $\cdot$ 5 $\mu$  (8); 515 $\mu$  (4); 513 $\mu$  (3); 506-509 $\mu$  (5); 504-504 $\cdot$ 5 $\mu$  (7); 475-477 $\mu$  (6).

*Urantetrafluorid* ( $\text{UF}_4$ ).

Bei +18°	Bei -180°	Bei +18°	Bei -180°
644-648 $\mu$ (10)	644-648 $\mu$ (10)	—	528 $\cdot$ 5-532 $\cdot$ 5 $\mu$ (4)
626-631 $\mu$ (6)	627-630 $\mu$ (8)	524-527 $\mu$ (4)	525 $\cdot$ 5-526 $\cdot$ 5 $\mu$ (4)
610-619 $\mu$ (3)	611-620 $\mu$ (2)	489-497 $\mu$ (3)	488-496 $\mu$ (3)
—	544-546 $\mu$ (4)	474-480 $\mu$ (3)	473-480 $\mu$ (3)
537-542 $\mu$ (4)	537-540 $\cdot$ 5 $\mu$ (4)		

*Urantetrachlorid* ( $\text{UCl}_4$ ).

Bei +18°	Bei -180°	Bei +18°	Bei -180°
658-664 $\mu$ (6)	{ 660-661 $\cdot$ 5 $\mu$ (9) 658-659 $\mu$ (8)	575-581 $\mu$ (3)	576-580 $\mu$ (3)
648-653 $\mu$ (10)	648 $\cdot$ 5-652 $\cdot$ 5 $\mu$ (10)	557 $\cdot$ 563 $\mu$ (8)	561-566 $\mu$ (5)
640-643 $\mu$ (5)	639-642 $\mu$ (8)	509-520 $\mu$ (5)	{ 519-519 $\cdot$ 5 $\mu$ (3) 514-515 $\mu$ (5) 510-511 $\mu$ (5)
630-633 $\mu$ (6)	629-632 $\mu$ (8)		
—	623-626 $\mu$ (1)	487 $\cdot$ 5-497 $\mu$ (4)	{ 494-495 $\mu$ (4) 490-491 $\mu$ (4)
—	619-622 $\mu$ (1)		
607-611 $\mu$ (8)	608-611 $\mu$ (7)	476-480 $\mu$ (3)	—
—	600-601 $\mu$ (3)		

*Urantetrabromid (UBr<sub>4</sub>).*

*Bei +18°:* 669-670 $\mu\mu$  (7); 660-663·5 $\mu\mu$  (10); 629-632 $\mu\mu$  (7); 620-626 $\mu\mu$  (7); 598-604 $\mu\mu$  (6); von 590 $\mu\mu$  an Totalabsorption.

*Bei -180°:* 661-662·5 $\mu\mu$  (10); 658-660 $\mu\mu$  (10); 648-650·5 $\mu\mu$  (9); 637-637·9 $\mu\mu$  (7); 629-631 $\mu\mu$  (7); 612-619·5 $\mu\mu$  (2); 620·5-627 $\mu\mu$  (2); 585 $\mu\mu$  (5); 575·5 $\mu\mu$  (6); 570·5 $\mu\mu$  (6); 520·5-522 $\mu\mu$  (5); 509-513 $\mu\mu$  (3); 498-501 $\mu\mu$  (3); 489-492 $\mu\mu$  (2).

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## Anwendung der Kryolyse auf Biologische Probleme.

VON

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### I. EINLEITUNG.

Gelegentlich der letzten Berliner Hauptversammlung der Deutschen Bunsen-Gesellschaft konnten wir, im Rahmen unserer Untersuchungen über den Mechanismus der Enzymwirkung, über die Kinetik der durch lebende Hefezellen bewirkten Zymasegärung berichten, (*Z. Elektrochem.*, 1929, **35**, 612; *Erg. Enzymforschung*, 1932, **1**, 77). Ihren Ursprung hatten diese Untersuchungen in der Beobachtung dass sich unter Einhaltung bestimmter physikalischer Bedingungen Lösungen herstellen lassen, in denen die im lyophil-kolloiden Zustand befindlichen Enzyme eine monatelange Wirksamkeit zeigten.

Entsprechend unserer früher geäusserten Hypothese (Nord, *Nature*, 1927, **120**, 82), wurde dann bei der weiterführung der Arbeiten festgestellt, dass an der Oberfläche der Teilchen der Enzymlösungen dieselben Gase adsorbiert bzw. in kolloid-chemisch sich verwandt verhaltenden Eialbumin—, Gummi arabicum —, Natriumoleat- und sonstigen Lösungen verzehrt werden können, die bei verschiedenen Zellreaktionen eine Erhöhung der enzymatischen Tätigkeit durch Steigerung der Zellpermeabilität bewirken. Die der Frostwirkung ausgesetzten Zymaselösungen zeigten ausser der verlangerten Haltbarkeit insofern eine auffallende Eigenschaft, als sie neben einer vorübergehend beträchtlich gesteigerten Gärfähigkeit einen Anstieg der Oberflächenspannung und ein Sinken der Viskosität aufwiesen. Die Veränderung beider Faktoren erreichte nach wenigen Tagen ein bestimmtes Maximum bzw. Minimum. Die bei der Vergärung von Glykose erzeugte Kohlensäuremenge stieg der massen, dass sie kurz nach Beendigung der "Induktionszeit" bis 6.6 ccm/min. betrug, um nachher bald auf das übliche Mass zurückzusinken. Die graduelle Steigerung hörte am 4. bis 5. Tage auf, um dann im Laufe der Hauptgärperiode praktisch gleichmässig zu bleiben.



TABELLE I.

Oberflächenspannung, Viskosität und entsprechende Gärgeschwindigkeit von gefrorenen Zymaselösungen.

Nach Tagen Frostwirkung.	Oberflächenspannung in Dyn/cm, bei 25°.	Relative Viskosität in Sek, bei 25°.	Entsprechende CO <sub>2</sub> Menge in 1 Minute.
0	41·45	80·80	4·4 **
1	43·67	79·1	4·8 **
3	45·89	78·4	2·3 †
5	42·93 *	76·4	2·4 †
15	42·93 *	76·2	2·1 †
28	44·41	76·7	2·2 †
57	44·41	76·4	1·2 †

Es war von Interesse, in diesen Versuchen festzustellen, dass die Spitzenleistung in der Gärfähigkeit dieser Zymaselösungen nach den ersten Minuten, unabhängig von der kaum veränderten Zuckerkonzentration, auf das übliche Mass zurückfiel. Daraus ergab sich der Schluss, dass die im Vergleich mit den sonst gewonnenen Lösungen vielleicht höher oberflächenwirksamen Zymasen gegen Proteolyse und produkte des Hefenstoffwechsels empfindlicher sind. Wenn also in einer biochemischen Reaktion das ideale Verhältnis zwischen wirksamer und unwirksamer Enzymmenge mit 1 angenommen wird, so wird im Laufe der Reaktion das Verhältnis zwischen wirksamen und "geschädigten" Enzymen mehr und mehr unter 1 sinken. Dieser Satz stützt sich natürlich auf die Annahme dass die Leistungen der Enzyme von ihrer Oberflächenwirksamkeit abhängig sind. Unmittelbar nach dem Reaktionsbeginn erleidet diese Oberfläche Veränderungen, infolge welcher die Geschwindigkeit der Reaktion sinkt, unabhängig von etwaigen Aenderungen der Substratkonzentration. Durch die Adsorbierbarkeit der für die früheren Versuche herangezogenen Gase konnte (a) die verschiebung des erwähnten Coeffizienten verzögert werden und (b) bei gleichzeitiger Instabilität des Adsorptionsfilms die Möglichkeit der "Schutzwirkung" dieser Verbindungen experimentell erhärtet werden.

Um die fruher (*Protoplasma*, 1928, 4, 547), gegebene Deutung zu vertiefen, stellten wir uns nunmehr zur Aufgabe, die einleitend er-

\* Das plötzliche Sinken ist die Folge einer vorübergehenden Temperaturerniedrigung im electrischen Kühlschrank; ein Teil der Enzymträger fiel dadurch aus und blieb auch nach dem Auftauen in Suspension.

\*\* Bei 1g. Glykose.

† Bei 0·5g. Glykose.

wähnte Beobachtung der Frostwirkung an kolloidchemisch verwandten, aber verhältnismässig definierten Lösungen bzw. Emulsionen einer ins Einzelne gehenden Untersuchung zu unterwerfen, zumal, trotz der unleugbaren Wichtigkeit der Kryolyse insbesondere lyophiler Kolloide für die Deutung von Vorgängen im Protoplasma bzw. in der tierischen und pflanzlichen Zelle überhaupt, dieser Gegenstand in den letzten Jahrzehnten eine kaum nennenswerte Bearbeitung vom physikalisch-chemischen Standpunkt aus gefunden hat.\* Ähnlich wie in einer unserer (Nord, *Ber.*, 1919, 52, 1705) früheren Untersuchungen handelt es sich also auch hier um einen Beitrag zur Deutung des physikalisch-chemischen Mechanismus einer Reaktion.

Bevor wir in die Beschreibung der Versuche bzw. Erörterung der Ergebnisse eintreten, müssen wir in Erinnerung zurückrufen, dass die Oberflächenspannungen der gefrorenen Zymaselösung erheblich anstiegen, die relativen Viskositäten sanken und die Kohlensäureerzeugung wiederum höher wurde. Voraussetzung für das Verständnis der ersten und dritten Gruppe der Erscheinungen dürfte unseres Erachtens, abgesehen von den Folgen einer denkbaren Dehydratisierung der Kolloidteilchen, die Möglichkeit sein, dass der Radius der lyophil-kolloiden Teilchen sich nach Einwirkung des Frostes verkleinert und dementsprechend ihre Oberfläche sich vergrößert hatte. Aber auch die Tatsache, dass die relativen Viskositäten in eindeutiger Weise durchgehend gesunken sind, müsste mit der erhöhten Oberflächenspannung bzw. der gesteigerten Kohlensäureerzeugung nicht in Widerspruch stehen, wenn wir (a) uns daran erinnern, dass die Zymaselösung im Vergleich z.B. mit einer Eiälbüminlösung keine homogene, sondern eine mehr an heterogene Systeme erinnernde Zusammensetzung besitzt, (b) daran denken, dass Variationen der Viskosität lyophiler Sole nach Kruyt, (*Kolloid Z.*, 1922, 31, 338), vielfach nicht der Änderung der Hydratation, sondern der geänderten elektrischen Ladung zuzuschreiben sind und (c) nicht übersehen, dass es Sole gibt, (Kruyt und Winkler, *Koll. Chem. Beih.*, 1931, 32, 375,) deren Viskosität mit der Zeit, wenn auch sehr wenig, aber regelmässig abnimmt.

\* H. M o l i s c h, Untersuchungen über das Erfrieren von Pflanzen, Jena 1897; P. B a c h m e t j e w, Experimentelle entomologische Studien vom physikalisch-chemischen Standpunkte aus, Bd. I, Leipzig 1901; A. L o t t e r m o s e r, *Z. physikal. Chem.*, 1907, 60, 462; E. F u l d und J. W o h l g e m u t h, *Biochem. Z.*, 1907, 5, 118; H. W. F i s c h e r, *Cohns Beitr. z. Biol. d. Pflanzen* 1911, 10, 183.

Wenn auch die Annahme von der durchgehenden Disaggregation der lyophil-kolloiden Teilchen unter der Einwirkung des Frostes auf den ersten Blick ungewöhnlich erscheint, aber nicht unwahrscheinlich ist, so erhob sich weiter die Frage nach einer Einheitlichkeit der Folgen der Frostwirkung auf den Dispersitätsgrad der Teilchen. Würden nämlich diese in den lyophil-kolloiden Lösungen unter dem Einfluss des Frostes lediglich eine Disaggregation erleiden, dann müssten sich sowohl Oberflächenspannung als auch Viskosität der Lösungen erhöhen. Sollte aber infolge der Frostwirkung sowohl eine Disaggregation als auch eine Aggregation (Vgl. die aggregierende Wirkung des Frostes z.B. auf den Erdboden: E. Jung, *Diss. Breslau*, 1931) der Teilchen eintreten, dann können Ueberdeckungen zustande kommen. Dies aber würde zur Folge haben, dass Oberflächenspannungen und Viskositäten verschieden gerichtete Veränderungen erleiden können bzw. es kann ein Teil der kolloiden Teilchen nach dem Auftauen aggregiert oder suspendiert bleiben, wodurch wohl die Erhöhung der Oberflächenspannung nicht verhindert wird, aber trotz vergrößerter Oberfläche ein Sinken der Viskosität eintreten kann.

Als Substrate unserer Messungen dienten: (1) Eialbumin-Lösungen, (2) Gelatinelösungen,\* (3) Gummi arabicum-Lösungen, (4) Lösungen von Saponin aus *Radix Saponaria* (Merck) mit 2.9% Aschengehalt, (5) Natriumoleat-Lösungen und (6) die mit Hilfe der vorgenannten Kolloide hergestellten Emulsionen von Olivenöl in Wasser. Bestimmend für diese Auswahl war, (a) dass nach den neuesten Ergebnissen der Enzymforschung die im krystallinen Zustand erhaltenen Enzyme wie z.B. Pepsin (Vgl. Northrop bzw. Sumner, *Erg., Enzymforschung*, 1932, 1, 295, 302), oder Urease eiweissartige Substanzen sein dürften. Eialbumin kann in Uebereinstimmung mit den Untersuchungsergebnissen von Sørensen (Mitt. vom Carlsberg Laboratorium, 12, 1915-17), bzw. Svedberg und Sjögren (*J. Amer. Chem. Soc.*, 1929, 51, 3594), als eine chemische Einheit mit dem Bence-Jones-Protein ähnlichen Eigenschaften betrachtet werden. (b) Im Gegensatz hierzu stellt Gelatine entsprechend den Befunden britischer Autoren (Hardy, *Proc. Roy. Soc.*, 1900, 66, 95; Lloyd, *Biochem. J.*, 1920, 14, 147;

\* Die Gelatine stammte von den Deutschen Gelatinewerken in Göttingen und wurde uns von der I. G. Farbenindustrie A. G. (Agfa) in dankenswerter Weise zur Verfügung gestellt.

Mardles, *Trans. Faraday Soc.*, 1930, **26**, 753), einen sowohl chemisch als auch physikalisch heterogenen Körper (Mol. Gew., 10,000-40,000; Vgl. Marinesco, *Compt. rend.*, 1931, **192**, 625), dar. (c und d) Sowohl Gummi arabicum als auch die Saponine gehören in die Gruppe der Glukoside mit der Massgabe, dass im Falle des Gummi arabicum die Hexosen bzw. Pentosen im allgemeinen an komplexe Säuren gebunden sind, wogegen die in den Saponinen befindlichen, an die Zucker gebundenen Reste Umwandlungsprodukte der Sterine darstellen. Bei den letzteren haben wir in der Zusammensetzung eine einfache Erklärung einerseits für ihre erhebliche Wasserlöslichkeit, andererseits für die starke Kapillaraktivität, (e) Im Gegensatz zu den Saponinen gehört Natriumoleat zu der Gruppe der kolloiden Elektrolyte.

## II. METHODEN UND APPARATE.

### A. Die Kryolyse.

Die in verschiedenen Konzentrationen angewandten Lösungen der lyophilen Kolloide wurden im allgemeinen der Frostwirkung bei  $-10^{\circ}$  bis  $-18^{\circ}$ ,  $-79^{\circ}$  und  $-180^{\circ}$  bei verschiedener Frierdauer ausgesetzt. Die Temperaturen wurden durch Verwendung einer Eiskochsalzmischung, fester Kohlensäure\* bzw. flüssiger Luft hergestellt. Es wurden Versuche zum raschen, zum langsamen und zum wiederholten Frieren einer Lösung angestellt. Die Messungen wurden immer an den eben aufgetauten Lösungen ausgeführt, wobei zu beachten ist, dass das Auftauen grundsätzlich bei Zimmertemperatur erfolgte. Bei den Emulsionen bestand keinerlei Beziehung zwischen dem Zeitpunkt der Herstellung der Emulsion und dem Zeitpunkt der Ausführung der Messung. Bei der Kryolyse der Lösungen, mittels derer die Emulsionen hergestellt wurden, kam die Temperatur bei  $-180^{\circ}$  auf Grund der später noch zu besprechenden Erfahrungen, die beider Messung der Lösungen selbst gewonnen worden waren, nicht zur Anwendung. Es ist also grundsätzlich zu beachten, dass wir nicht fertige Emulsionen der kryolyse unterworfen haben.

\* Für die Bereitstellung der festen Kohlensäure sind wir dem Ammoniakwerk Merseburg, Leunaerke, zu Dank verpflichtet.

## B. Messmethoden.

1. Die Bestimmung der Oberflächenspannungen der Lösungen wurde bei Zimmertemperatur mit dem Tensiometer Von Du-Nöuy, wie von Nord und Franke (*loc. cit.*) angegeben, ausgeführt. Die Messungen der Oberflächenspannungen an Emulsionen und an den 1-bzw. 2-prozentigen Lösungen, mittels derer die Emulsionen hergestellt waren, wurden mit einem geraden Stalagnometer nach Traube ausgeführt; Das Stalagnometer wurde mit einer aufgesetzten Kapillare versehen so dass 5 ccm. destilliertes Wasser bei einer Temperatur von 22° in 48 Tropfen ausflossen.

2. Die Viskositäten der Lösungen wurden im Wasserthermostaten bei 22° im Ostwald-Viskosimeter bestimmt. Die Ergebnisse sind in den Tabellen als relative Viskositäten, bezogen auf Wasser gleicher Temperatur, angegeben. Die Viskosität der Emulsionen und der hierher gehörigen 1-bzw. 2-proz. Lösungen wurden im Wasserthermostaten bei 18° im Vogel-Ossag-Viskosimeter gemessen. Diese Ergebnisse sind in den Tabellen als absolute Fließzeiten in Sekunden angegeben.

3. Bestimmung der Leitfähigkeit.—Die elektrische Leitfähigkeit wurde nach der Methode von Kohlrausch mit Wechselstrom und Telephon gemessen. Die Widerstandskapazität des Widerstandsgefäßes betrug im Falle der Lösungen  $C=0.2900$  bei 22°, im Falle der Emulsionen und der dazu gehörigen Lösungen 0.312 bei 18°. Die Messungen wurden mit je 20 ccm. der ungefrorenen bzw. gefrorenen Lösungen und Emulsionen ausgeführt. Zur Kontrolle wurde jede Messung mit zwei Vergleichswiderständen verschiedener Stärke je zwei—bis drei Mal nachgeprüft. Trotz der geringen Leitfähigkeit der Eialbumin—bzw. Gummi arabicum—Lösungen wurden die Widerstände so gewählt, dass die Messungen möglichst in der Mitte der Wheatstone-schen Brücke ausgeführt werden konnten. Grundbedingung für die Erzielung reproduzierbarer Werte bei der Messung der Leitfähigkeit der in unseren Versuchen angewandten und unter den beschriebenen Bedingungen hergestellten Emulsionen war, dass die Emulsionen bis zum Augenblick der Ablesung des gemessenen Widerstandes gleichmässig und ohne Unterbrechung gerührt wurden. Unterblieb das Rühren oder wurde es frühzeitig abgebrochen, so konnte, im richtigen Gegensatz zu den Erfahrungen von Fricke und Morse (*Physical Rev.*,

1926, 25, 365), ein Steigen der Leitfähigkeit wahrgenommen werden. Dieses ist ohne weiteres verständlich, wenn wir uns klar machen, dass mit dem Einstellen des Rührons das Aufrahmen der Emulsionen einsetzt und hiermit eine Anreicherung des leitenden Emulgators in der Umgebung der Messelektrode beginnt.

4. Bestimmung der kataphoretischen Wanderungsgeschwindigkeit.—Grössere Schwierigkeiten bot die Bestimmung der kataphoretischen Wanderungsgeschwindigkeit kolloider Teilchen im elektrischen Felde. Es wäre wünschenswert gewesen, hierzu die sorgfältig durchgearbeitete Methode des Svedberg'schen Laboratoriums (Vgl. Tiselius, *Nova Acta R. Soc. Sci. Upsaliensis*, 1930, iv, 7, Nr. 4), anzuwenden. Von dieser Absicht mussten wir aber mangels einer geeigneten Vorrichtung zum Photographieren der wandernden Grenzschichten absehen. Eine für die Ergebnisse gleichwertige, in der Ausführung jedoch etwas einfachere Methode haben Bendien und Janssen (*Rec. Trav. Chim.*, 1927, 46, 739; 1928, 47, 1042) angegeben. Die Apparatur bestand aus einer modifizierten Burton'schen Zelle mit einer Elektrodenentfernung von etwa 40 mm, die zum guten Temperatúrausgleich in einem mit Wasser gefüllten Thermostaten benützt wurde. Die Messungen wurden bei 19° ausgeführt. Mit Hilfe einer Lupe war es möglich, die Lage der Grenzflächen bis auf 0.1 mm zu schätzen. Es gelang uns, die Grenzflächen bereits mit einer kleinen Bogenlampe, die über dem Apparat befestigt war, und die ihr Licht direkt auf die Grenzflächen warf, sichtbar zu machen. Es genügten für jede Bestimmung 7 ccm der kolloiden Lösung. Auf diese Weise war es möglich, die Wanderungsgeschwindigkeiten gefrorener und ungefrorener Eialbumin— bzw. Gelatinelösungen zu bestimmen (Vgl. Nord, *Erg. Enzymforsch.*, 1932, 1, 82). Dagegen gelang es uns nicht, die Grenzfläche bei einer Gummi arabicum-Lösung sichtbar zu machen. Bei jeder Lösung mussten erst die der jeweiligen Konzentration der kolloiden Lösung am besten entsprechenden Einflusszeiten in Blindversuchen bestimmt werden, um eine sich deutlich abhebende Grenzfläche zu erhalten. Die Messdauer betrug im Durchschnitt 120 Minuten; abgelesen wurde alle 15–20 Minuten, und die Versuchsdauer so lange ausgedehnt, bis die Grenzflächen undeutlich wurden. Diese Erscheinung trat bei allen gefrorenen Lösungen (ausser der einprozentigen Eialbuminlösung) regelmässig 15–20 Minuten früher ein, als bei den ungefrorenen, so dass hierdurch jede Messung aus 6–7 Ablesungen bestand.

Sämtliche Lösungen wurden mit Leitfähigkeitswasser hergestellt. Die Eigenleitfähigkeit des Wassers wurde selbstverständlich von den gefundenen Werten in Abzug gebracht; die des Olivenöls war unterhalb der Messgrenze unserer Apparatur und wurde deshalb vernachlässigt. Die ungefrorenen Eialbuminlösungen wurden unter Toluol aufbewahrt. Das verwendete Gummi arabicum war ein Kahlbaum-Präparat DAB 6. Mit Rücksicht auf dessen Empfindlichkeit für Elektrolyte (K r u y t und T e n d e l o o, *Koll. Chem. Beih.*, 1929, 29, 400) haben wir von einer Entfernung der Asche abgesehen. Die von uns verwendeten Sole waren glasklar. Es zeigte sich in ihnen auch nach monatelanger Aufbewahrung bei Zimmertemperatur weder irgendeine Fällung noch bakterielle Einwirkung. Die Konzentration der Lösungen bewegte sich im Bereich von  $1-10^{-6}$  Proz. Die Konzentration der Eialbuminlösungen wurde durch Zurückwägen des vorher durch Abzentrifugieren abgetrennten ungelösten Trockenrückstandes der Einwage bestimmt. Sämtliche Emulsionen wurden mit Olivenöl hergestellt, das einen Gehalt von 0.4% freier Säure, berechnet als Oelsäure, enthielt. Zur Emulgierung wurden 2%, bei Natriumoleat 1 per cent. der Emulgatoren in wässriger Lösung verwendet. Die Emulsionen enthielten jeweils 10 % Olivenöl, berechnet auf die fertiggestellte Emulsion. Brauchbare Emulsionen unter Verwendung einer Schüttelmaschine konnten nur mit Natriumoleat als Emulgator hergestellt werden. Um auch mit den anderen von uns herangezogenen Emulgatoren stabile Emulsionen herzustellen, bedienten wir uns einer H u r r e l l-Laboratoriums-Homogenisiermaschine,\* die im Mittel eine Tourenzahl von 9000/min besitzt. Die Homogenisierung wurde fünf Mal hintereinander wiederholt.

### III. ZUSAMMENHANG ZWISCHEN FROSTWIRKUNG UND OBERFLÄCHENSPIGEL- CHENSPIGEL-SPANNUNG BZW. VISKOSITÄT.

#### A. Eialbumin-Lösungen und -Emulsionen.

Die Kryolyse der Eialbuminlösungen wurde in der Weise ausgeführt, dass sie der Frostwirkung (a) von verschiedener Dauer, (b) wiederholt und (c) bei verschiedenen Temperaturen ausgesetzt wurden.

\* Für die leihweise Ueberlassung sind wir der Herstellerin, der Maschinenfabrik Wilh. G. Schröder Nachf. A.G., Lübeck zu besonderem Dank verpflichtet.

TABELLE II a.

*Oberflächenspannung von Eialbuminlösungen in Dyn/cm,  
b. 20°, b. verschiedener Frierdauer.*

K

Konzentration.	Gefroren bei -18°						Ungefroren.
	2 Stden.	4 Stden.	16 Stden.	24 Stden.	31 Stden.	48 Stden.	
0·1 %	57	58	60	61	61·2	61·9	54·7
0·01 %	64·9	64·9	65	65	66·3	67·3	62·8
0·001 %	73·5	73·5	73·6	73·6	74	76·3	70
0·005 %	60·1	61·3	63	63·9	65·7	69·1	58·4
0·0001 %	72·8	73	73·9	74·7	76·6	77·9	70·9

TABELLE II b.

*Oberflächenspannung von Eialbuminlösungen in Dyn/cm,  
b. 20°, nach wiederholtem Frieren und verschiedener  
Frierdauer.*

Konzentration.	Ungefroren.	Gefroren bei -18°	
		zweimal je 2 Stden.	dreimal (2 mal 2 Stden, 1 mal 48 Stden).
0·1 %	54·7	57·3	57·5
0·01 %	62·8	65	65·2
0·001 %	70	73·5	73·5
0·0001 %	70·9	73	

TABELLE II c.

*Oberflächenspannung von Eialbuminlösungen in Dyn/cm,  
b. 20°, nach Einwirkung tieferer Temperaturen  
bei verschiedener Frierdauer.*

Konzentration.	Ungefroren.	gefroren		
		2 Stden b. -79°.	24 Stden b. -79°.	2 Stden b. -150°.
0·1 %	54·7	65	65	61
0·01 %	62·8	69·1	69·9	68·4
0·001 %	70	76	76·1	74·9
0·0001 %	70·9	78·1	...	77·4



TABELLE II d.

*Tropfenzahl einer Eialbumin-Lösung bzw.—Emulsion,  
gemessen im Stalagmometer bei 22°.*

	ungefroren.	2 Std. gefroren	
		bei, -18°.	bei, -79°.
2 proz. Lösung	48 Tropfen	52 Tropfen	52 Tropfen
Emulsion	67 Tropfen	73 Tropfen	74 Tropfen

(a) Aus den in den Tabellen wiedergegebenen und wiederholt kontrollierten Werten geht eindeutig hervor, dass die Oberflächenspannungswerte in allen Konzentrationen bei der gleichen Frieretemperatur von -18° mit der Frierdauer steigen. Mit sinkender Konzentration steigert sich im allgemeinen die Fähigkeit der Lösungen, ihre Oberflächenspannung zu erhöhen. Dies gilt mit der Einschränkung, dass es 1. in die Tabelle nicht aufgenommene Zwischenkonzentrationen gibt, bei denen die Veränderung der Oberflächenspannung keine messbaren Unterschiede in Bezug auf die nächst höhere Konzentration aufweist, und 2. die Verschiebungen der Oberflächenspannungswerte stark verdünnter Eialbuminlösungen, wenn sie schon bei den ungefrorenen Lösungen in grosser Nähe des Wasserwertes liegen, nur einen auch absolut geringeren Anstieg zeigen.

(b) Wiederholtes Frieren derselben Lösung, bei verschiedener Frierdauer und sogar bei verschiedener Temperatur führt zu keiner Änderung der beim erstmaligen Frieren erreichten Oberflächenspannungswerte.

(c) Wird eine Lösung z. B. bei -79°, also sehr rasch gefroren, so weist die aufgetaute Lösung unabhängig von der Frierdauer von 2 bis 24 Stunden keine nennenswerte Erhöhung der gemessenen Oberflächenspannungswerte, verglichen mit den Höchstwerten der bei -18° gefrorenen Lösungen gleicher Konzentration, auf. Die erreichten Oberflächenspannungswerte sind zum Teil (bei höheren Konzentrationen) nur um ein Geringes höher, zum Teil (bei sinkender Konzentration auf gleicher Höhe wie der höchste bei -18° erreichte Wert. Die Oberflächenspannungswerte der bei -180° gefrorenen Lösungen bleiben durchweg unterhalb der Werte, die an bei -79° gefrorenen Lösungen gemessen wurden.

(d) Entsprechend der Tatsache, dass sich mit steigender Konzentration die Hydratation der lyophilen Kolloide stets verringert, sehen wir, im richtigen Gegensatz zu den in den obigen Tabellen

mitgeteilten Ergebnissen, dass die aus den Tropfenzahlen zu schliessenden Oberflächenspannungen durchwegs gesunken sind.

Die Viskositätsbestimmungen wurden an einem anderen Teil derselben und ebenso behandelten Lösungen ausgeführt.

TABELLE III a.

*Relative Viskosität von Eialbuminlösungen b. 22·2°, bei verschiedener Frierdauer.*

Konzentration.	Ungefroren.	bei -18°, gefroren					
		2 Stden.	4 Stden.	16 Stden.	24 Stden.	31 Stden.	48 Stden.
0·1%	1·024	1·033	1·035	1·046	1·051	1·059	1·090
0·01%	1·018	1·031	1·033	1·035	1·046	1·049	1·075
0·001%	1·016	1·029	1·029	1·040	1·044	1·055	1·072
0·005%	1·009	1·011	1·011	1·011	1·012	1·012	1·014
0·0001%	1·003	1·016	1·020	1·036	1·042	1·051	1·068

TABELLE III b.

*Relative Viskosität von Eialbuminlösungen b. 22·2°, nach wiederholtem Frieren bei verschiedener Frierdauer.*

Konzentration.	Ungefroren.	Gefroren bei -18°	
		2 mal je 2 Stden.	3 mal (2 mal je 2 Stden, 1 mal 48 Stden).
0·1%	1·024	1·035	1·038
0·01%	1·018	1·033	1·035
0·001%	1·016	1·035	1·035
0·0001%	1·003	1·036	—

TABELLE III c.

*Relative Viskosität von Eialbuminlösungen b. 22·2°, nach Einwirkung tieferer Temperaturen bei verschiedener Frierdauer.*

Konzentration.	Ungefroren.	gefroren		
		2 Stden b. -79°.	24 Stden b. -79°.	2 Stden b. -180°.
0·1%	1·024	1·030	1·030	1·031
0·01%	1·018	1·073	1·075	1·060
0·001%	1·016	1·072	1·072	1·059
0·0001%	1·008	1·062	—	1·053

TABELLE III d.

*Viskositäten einer Eialbumin-Lösung bzw.—Emulsion bei 18°.*

	Ungefroren.	2 Std. gefroren	
		bei -18°.	bei -79°.
2 proz. Lösung	20·6 sec	20·4 sec	20·2 sec
Emulsion	21·4 sec	20·7 sec	21·2 sec

(a) In guter Uebereinstimmung mit den Oberflächenspannungswerten ist aus den in den vorstehenden Tabellen wiedergegebenen Viskositätswerten eine parallele Erhöhung der Viskosität der gefrorenen Lösungen, verglichen mit den ungefrorenen Lösungen, festzustellen. Die Viskositätswerte steigen jedoch bei Lösungen sinkender Konzentration nicht (wie die Werte der Oberflächenspannung) stärker.

(b) Mehrfaches Frieren verursacht, in Uebereinstimmung mit den unveränderten Werten der Oberflächenspannung, keine weitere Aenderung der Viskositätswerte.

(c) Auch in diesem Falle verändern sich die Viskositätswerte in Uebereinstimmung mit den Oberflächenspannungswerten.

(d) Die Viskositätswerte sinken in Uebereinstimmung mit dem Rückgang der aus den Tropfenzahlen zu schliessenden Oberflächenspannungswerte.

Aus den in den Tabellen II d und III d zusammengestellten Werten geht in Uebereinstimmung mit der dort zur Anwendung gelangten Konzentration des Eialbumins und im Gegensatz zu den in den Tabellen II a-c bzw. III a-c mitgeteilten Werten von Messungen aus vielfach niedrigeren Konzentrationsbereichen—hervor, dass sowohl die Oberflächenspannungs—als auch die Viskositätswerte sich im Vergleich zu den an den entsprechenden ungefrorenen Lösungen bzw. Emulsionen erhaltenen Werten verringert haben. Dieser Gegensatz ist selbstverständlich, wenn wir die mit steigender Konzentration parallel laufende Verringerung der Hydratation in Betracht ziehen. Bereits in unseren früheren Versuchen über die Gasverzehrung (*Z. phys. Chem.*, 1930, **A**, 150, 12; *Trans. Faraday Soc.*, 1930, **26**, 760) bzw. den Einfluss von Gasen auf die Oberflächenspannung usw. lyophiler Kolloide \* haben wir darauf hingewiesen

\* Auf diese verhältnisse bzw. den Einfluss der Teilchen grösse auf die diffusion in verbindung mit der kroylyse auch einfacherer chemisch definierter verbindungen wird noch Zurückzukommen sein.

dass der Anstieg der Teilchengrösse mit einer Oberflächenverringern parallel geht. Die durch den Frost bewirkte Disaggregation-Aggregation kolloider Teilchen ist in diesem Konzentrationsbereich, entsprechend der zunehmenden Association der kolloiden Eialbumin-teilchen, wesentlich zugunsten der Aggregation verschoben, dies um so eher, wenn wir der S t a u d i n g e r schen (*Ber.*, 1929, **62**, 2893) auffassung beipflichten, dass die Eiweisskolloide lediglich Riesen moleküle von kolloidem Ausmass darstellen, d.h. nicht micellar sind. Eine etwaige Aggregation kann natürlich bis zu einer Koagulation fortschreiten, und dementsprechend wird die gesunkene Oberflächenspannung von einer gesunkenen Viskosität begleitet sein. Diese Verhältnisse werden am besten durch das nachfolgende Abbildungspaar (Abb. 1 und 2) illustriert. Die beiden Aufnahmen stellen Mikrophotogramme\* etwa 100 fach vergrösserter Emulsionen dar. Abb. 1 gibt die Teilchen der mit einem bei  $-79^{\circ}$  gefrorenen und wieder aufgetauten Emulgator hergestellten Emulsion und Abb. 2 gibt die Teilchen der mit einem ungefrorenen Emulgator hergestellten Emulsion wieder. Die infolge Vergrösserung der Tröpfchen offenkundige Oberflächenverringern ist ohne weiteres zu ersehen.

Bevor wir in die Besprechung der an anderen Kolloiden erhaltenen Ergebnisse eintreten, sei mit Rücksicht auf die späteren theoretischen Erörterungen darauf hingewiesen, dass die Stammlösungen bei längerem Stehen einen geringen, aber gut messbaren Anstieg der Oberflächenspannungswerte aufweisen, ohne jedoch den Wasserwert auch bei den stärksten Verdünnungen im Gegensatz zu der Aussage von C l a r k und M a n n (*J. Biol. Chem.*, 1922, **52**, 180; vgl. auch Y i n g F u und H s i e n W u, *Proc. Soc. Exp. Biol. Med.*, 1930, **27**, 878)—jemals zu überschreiten, und dass sich eine nach dem Gefrieren aufgetaute Eialbuminlösung im Aussehen in keiner Weise von der Stammlösung unterscheidet.

#### B. Gelatinelösungen.

Die Kryolyse der Gelatinelösungen wurde unter den gleichen Bedingungen wie die der Eialbuminlösungen ausgeführt.

\* Für die Anfertigung dieser und der nachfolgenden Mikrophotogramme sind wir der I. G. Farbenindustrie A. G. (Agfa) zu besonderem Dank verpflichtet.

TABELLE IV a.

*Oberflächenspannung von Gelatinelösungen in Dyn/cm, b. 20°, b. verschiedener Frierdauer.*

Konzentration.	Ungefroren.	Gefroren bei -18°				
		2 Stden.	4 Stden.	16 Stden.	31 Stden.	48 Stden.
0.5%	50.2	52.9	52.9	53.1	53.8	54.2
	69.3	70	70.2	70.5	72	74.6
0.01%	59.7	61.9	62.1	63.3	63.3	64.1
	70	70.6	70.9	71	71.9	75.8
0.001%	67.3	69.8	70.1	70.9	71.7	75.3
	73.4	73.8	73.9	73.9	74.5	76.6
0.0001%	75.9	76.6	76.6	76.9	77.3	77.6

TABELLE IV b.

*Oberflächenspannung von Gelatinelösungen in Dyn/cm, b. 20°, nach wiederholtem Frieren bei verschiedener Frierdauer.*

Konzentration.	Ungefroren.	Gefroren bei -18°	
		2mal je 2 Stden.	3mal (2 mal je 2 Stden, 1mal 48 Stden).
0.5%	50.2	53	53
	69.3	70	70.2
0.01%	59.7	62	62.1
	70	70.9	70.9
0.001%	67.3	70	70

TABELLE IV c.

*Oberflächenspannung von Gelatinelösungen in Dyn/cm, b. 20°, nach Einwirkung tieferer Temperaturen bei verschiedener Frierdauer.*

Konzentration.	Ungefroren.	Gefroren		
		2 Stden b. -79°.	24 Stden b. -79°.	2 Stden b. -180°.
0.5%	50.2	53.8	53.9	53.0
	69.3	74.6	75.0	73.5
0.01%	59.7			62.3
	70.0	74.5	75.0	73.6
0.001%	67.3			70.8
	73.4	76.5		75.9
0.0001%		77.3	77.3	76.0

(a) und (b). Die in diesen Tabellen wiedergegebenen Veränderungen der Oberflächenspannungswerte bzw. Richtungen der Veränderungen entsprechen vollkommen den Werten, die in den Tabellen der Oberflächenspannungswerte für Eialbuminlösungen mitgeteilt sind, mit der Einschränkung, dass die absolute Erhöhung der Oberflächenspannungswerte etwas geringer ist. Dementsprechend ist bei sinkender Konzentration die Steigerung geringer. Das gleiche trifft auch für die Folgen des wiederholten Frierens zu. Die schon bei den Eialbuminlösungen erwähnte Beobachtung, dass die ungefrorenen Lösungen bei längerem Stehen einen Anstieg der Oberflächenspannungswerte zeigen, bestätigte sich an den Gelatinelösungen und traf hier in noch höherem Masse zu. In dieser Tabelle sind die Oberflächenspannungswerte der Lösungen am Anfang und am Ende der Versuchsperiode aufgenommen. Es lässt sich daraus klar ersehen, dass 1. mit der Zeit eine nicht unwesentliche Erhöhung der Oberflächenspannungswerte der ungefrorenen Lösungen erfolgt ist, und dass 2., je näher der Oberflächenspannungswert der ungefrorenen Lösungen zu dem Oberflächenspannungswert des Wassers liegt, um so weniger infolge der Frostwirkung eine weitere Erhöhung der Oberflächenspannungswerte eintritt.

(c) Die Oberflächenspannungswerte, die nach dem raschen Ausfrieren der Lösung bei  $-79^{\circ}$  bzw. bei  $-180^{\circ}$  beobachtet wurden, erreichen die höchsten Werte, die an bei  $-18^{\circ}$  gefrorenen Lösungen gemessen wurden, nicht.

Aus der unten folgenden Zusammenstellung der Ergebnisse der Viskositätsmessungen an Gelatinelösungen geht eindeutig hervor, dass sowohl im

TABELLE V a.

*Relative Viskosität von Gelatinelösungen b.  $22.2^{\circ}$ , b. verschiedener Frierdauer.*

Konzentration.	Ungefroren.	Gefroren b. $-18^{\circ}$				
		2 Stden.	4 Stden.	16 Stden.	31 Stden.	48 Stden.
0.5%	1.160	1.153	1.153	1.144	1.082	1.077
0.01%	1.081	1.078	1.048	1.029	1.025	1.025
0.001%	1.062	1.042	1.040	1.030	1.025	0.990
0.0001%	0.994	0.977	0.975	0.961	0.955	0.903

TABELLE V b.

*Relative Viskosität von Gelatinelösungen b. 22·2°, nach wiederholtem Frieren bei verschiedener Frierdauer.*

Konzentration.	Ungefroren.	Gefroren bei -18°	
		2 mal je 2 Stden.	3 mal (2 mal je 2 Stden, 1 mal 48 Stden).
0·5%	1·160	1·153	1·151
0·01%	1·091	1·052	1·049
0·001%	1·062	1·025	1·025
0·0001%	0·994	0·977	0·974

TABELLE V c.

*Relative Viskosität von Gelatinelösungen b. 22·2°, nach Einwirkung tieferer Temperaturen bei verschiedener Frierdauer.*

Konzentration.	Ungefroren.	Gefroren		
		2 Stden b. -79°.	24 Stden b. -79°.	2 Stden b. -180°.
0·5%	1·160	1·077	1·077	1·086
0·01%	1·091	1·026	...	1·043
0·001%	1·062	0·995	...	1·008
0·0001%	0·994	0·918	...	0·947

Gegensatz zur Steigerung der Oberflächenspannungswerte als auch zur Steigerung der Viskositätswerte bei den Eialbuminlösungen die Viskositätswerte der gefrorenen Gelatinelösungen durchweg unter den Werten der ungefrorenen Stammlösung liegen. Wiederholtes Frieren und auch Frieren bei tieferen Temperaturen verursacht keine weitere Veränderung der Viskositätswerte; in diesem Punkt stimmen die Beobachtungen bei Gelatinelösungen und bei Eialbuminlösungen miteinander überein.

C. *Gummi arabicum*—Lösungen und—Emulsionen.

TABELLE VI a.

*Oberflächenspannung von Gummi arabicum*lösungen in Dyn/cm, b. 20°, b. verschiedener Frierdauer.

Konzentration.	Ungefroren.	Gefroren bei—18°				
		2 Stden.	16 Stden.	24 Stden.	31 Stden.	48 Stden.
0·1%	64·70 schwankend	71	61·9	72·5	72·7	72·9
0·01%	72·5	73	73·7	74·8	75	77·5
0·001%	73·3	74·1	74·5	75·1	75·9	78·3
7·0%	61·5	63·1	63·7	63·9	64·8	68·2
	69	70			71·1	71·5

TABELLE VI b.

*Oberflächenspannung von Gummi arabicum* Lösungen in Dyn/cm b. 20°, nach wiederholtem Frieren bei verschiedener Frierdauer.

Konzentration.	Ungefroren.	Gefroren bei—18° 2 mal (je 1 mal 2 Stden 48 Stden).	
0·1%	64·70		71·2
0·01%	72·5		73·2
0·001%	73·3		74·3
7·0%	61·5		63·5

TABELLE VI c.

*Oberflächenspannung von Gummi arabicum* Lösungen in Dyn/cm, b. 20°, nach Einwirkung tieferer Temperaturen bei verschiedener Frierdauer.

Konzentration.	Ungefroren.	Gefroren		
		2 Stden b.—79°.	24 Stden b.—79°.	2 Stden b.—180°.
0·1%	64·70	77·7	77·7	76·9
0·01%	72·5	77·2	77·2	77
0·001%	73·3	78·1	...	77·6
7·0%	61·5	67·9	68	67·1



TABELLE VI d.

*Tropfenzahlen einer Gummi arabicum-Lösung bzw.-Emulsion,  
gemessen in Stakgmometer bei 22°.*

	Ungefroren.	2 Std. gefroren	
		bei, -18°.	bei, -79°.
2 proz. Lösung	45 Tropfen	44 Tropfen	43 Tropfen
Emulsion	61 Tropfen	60 Tropfen	57 Tropfen

TABELLE VII a.

*Relative Viskosität von Gummi arabicum Lösungen b. 22·2°, b  
verschiedener Frierdauer.*

Konzentration.	Ungefroren.	Gefroren bei, -18°				
		2 Stden.	16 Stden.	24 Stden.	31 Stden.	48 Stden.
0·1%	1·062	1·038	1·032	1·012	1·003	0·989
0·01%	1·028	1·028	1·019	1·012	1·009	0·955
0·001%	1·019	1·012	1·009	1·007	1·003	0·956
7·0%	3·606	3·510	3·480	...	3·279	3·259

TABELLE VII b.

*Relative Viskosität von Gummi arabicum Lösungen b. 22·2°  
nachwiederholtem Frieren bei verschiedener Frierdauer.*

Konzentration.	Ungefroren.	gefroren b. -18°	
		2 mal (je 1 mal 2 Stden. 48 Stden).	
0·1%	1·062	1·062	
0·01%	1·028	1·022	
0·001%	1·019	1·009	
7·0%	3·606	34·9	

TABELLE VII c.

*Relative Viskosität von Gummi arabicum Lösungen b. 22·2°  
nach Einwirkung tieferer Temperaturen bei verschiedener Frierdauer*

Konzentration.	Ungefroren.	Gefroren		
		2 Stden b. -79°.	24 Stden b. -79°.	2 Stden b. -180°.
0·1%	1·62	0·994	0·994	0·996
0·01%	1·028	0·964	0·952	0·969
0·001%	1·019	1·008	--	0·956
7·0%	3·606	3·885	3·884	3·887

TABELLE VII d.

*Viskositäten einer Gummi arabicum-Lösung bzw.  
Emulsion bei 18°.*

	Ungefroren.	2 Std. gefroren	
		bei -18°.	bei -79°.
2 proz. Lösung	36·4 sec	36·8 sec	37·6 sec
Emulsion	35·6 sec	36·2 sec	38·4 sec

Die an gefrorenen Gummi arabicum-Lösungen gemachten Beobachtungen hinsichtlich der Veränderungen der Werte der Oberflächenspannung bzw. Viskosität entsprechen in qualitativer Beziehung den an Gelatinelösungen gemachten Feststellungen. Lediglich die Viskositätswerte der konzentrierten Gummilösungen sowie die der betreffenden Emulsionen bewegen sich in entgegengesetzter Richtung. Bei allen Lösungen konnten die Messungen einwandfrei reproduziert werden, mit Ausnahme der 0·1 proz. ungefrorenen Lösung, die starke Schwankungen aufwies, die aber unter dem Einfluss des Frostes aufhörten.

#### D. Saponin-Lösungen und Emulsionen.

TABELLE VIII.

*Tropfenzahlen einer Saponin-Lösung bzw. -Emulsion, gemessen  
im Stalagmometer bei 22°.*

	Ungefroren.	2 Std. gefroren	
		bei -18°.	bei -79°.
2 proz. Lösung	55 Tropfen	51 Tropfen	49 Tropfen
Emulsion	75 Tropfen	66 Tropfen	62 Tropfen

TABELLE IX.

*Viskositäten einer Saponin-Lösung bzw. -Emulsion bei 18°.*

	Ungefroren.	2 Std. gefroren.	
		bei -18°	bei -79°
2proz. Lösung	19·8 sec	20·2 sec	20·6 sec
Emulsion	20·2 sec	23·4 sec	20·7 sec

Sowohl die aus den Tropfenzahlen zu schliessenden Oberflächenspannungswerte als auch die Viskositätswerte zeigen bei den Lösungen wie bei den mit ihnen hergestellten Emulsionen ein Ansteigen, verglichen mit den betreffenden werten der ungefrorenen Ausgangspräparate.

Nach den unten folgenden Mikrophotogrammen zu urteilen die mit (Abb. 3 und 4) bei -79° gefroren gewesenen bzw. mit ungefroren Saponinlösungen hergestellte Emulsionströpfchen darstellen, hat sich die Oberfläche der ersteren um ein Mehrfaches vergrössert.

E. Natriumoleat-Lösungen und -Emulsionen.

TABELLE X a.

*Oberflächenspannung von Natriumoleatlösungen in Dyn/cm, b. 20° bei verschiedener Frierdauer.*

Konzentra- tion.	Ungefro- ren.	Gefroren bei -18°					
		2 Stden.	4 Stden.	16 Stden.	24 Stden.	31 Stden.	48 Stden.
5%	52	52·8	52·9	53·5	53·75	54·1	54·9
0·1%	30·5	31·9	33·1	33·1	34	34·5	34·5
0·01%	36·1	38	38·73	39·1	40·4	42	42
0·001%	39·9	42	42	42·5	42·7	43·1	44
0·0001%	60·2	62	62·16	62·9	63·6	63·7	64·6

TABELLE X b.

*Oberflächenspannung von Natriumoleatlösungen in Dyn/cm, b. 20° nach wiederholtem Frieren bei Verschiedener Frierdauer.*

Konzentration.	Ungefroren.	Gefroren bei -18°	
		2 mal je 2 Stden.	3 mal (2 mal je 2 Stden, 1 mal 48 Stdevl.)
5%	52	52·8	52·8
0·1%	30·5	32·1	32·1
0·01%	36·1	39·1	39·1
0·001%	39·9	42	42
0·0001%	60·2	62·1	62·1

TABELLE X c.

*Oberflächenspannung von Natriumoleatlösungen in Dyn/cm, b. 20°  
nach Einwirkung tieferer Temperaturen.*

Konzentration.	Ungefroren.	Gefroren	
		2 Stden b. -79°.	2 Stden b. -180°.
5%	52	54	54
0.1%	30.5	34.5	34.1
0.01%	36.1	42.4	41.1
0.001%	39.9	44	42.5
0.0001%	61.2	64.2	63.9

TABELLE X d.

*Tropfenzahlen einer Natriumoleat-lösung bzw.-Emulsion,  
gemessen im Stalagmometer bei 22°.*

	Ungefroren.	2 Std. gefroren	
		bei -18°.	bei -79°.
2 proz. Lösung	143 Tropfen	140 Tropfen	142 Tropfen
Emulsion	99 Tropfen	97 Tropfen	99 Tropfen

TABELLE XI a.

*Relative Viskosität von Natriumoleatlösungen b. 22.2° bei  
verschiedener Frierdauer.*

Konzentra- tion.	Ungefro- ren.	Gefroren bei -18°					
		2 Stden.	4 Stden.	16 Stden.	24 Stden.	31 Stden.	48 Stden.
5%	2.521	2.149	2.149	2.149	2.144	2.144	2.144
0.1%	1.038	1.038	1.038	1.035	1.035	1.033	1.033
0.01%	1.020	1.020	1.022	1.022	1.022	1.024	1.025
0.001%	1.016	1.016	1.016	1.031	1.031	1.031	1.031
0.0001%	0.979	0.979	0.979	0.959	0.957	0.957	0.944

TABELLE XI b.

*Relative Viskosität von Natriumoleatlösungen b. 22·2° nach  
wiederholtem Frieren bei verschiedener Frierdauer.*

Konzentration.	Ungefroren.	gefroren b. -18° 2 mal (je 1 mal 2 Stden und 48 Stden).
0·1%	1·038	1·038
0·01%	1·020	1·020
0·001%	1·016	1·016

TABELLE XI c.

*Relative Viskosität von Natriumoleatlösungen b. 22·2° nach  
Einwirkung tieferer Temperaturen.*

Konzentration.	Ungefroren.	gefroren	
		2 Stden b. -79°.	2 Stden b. -180°.
5%	2·521	2·975	3·133
0·1%	1·038	1·33	1·035
0·01%	1·020	1·025	1·024
0·001%	1·016	1·035	1·031
0·0001%	0·979	0·942	0·940

TABELLE XI d.

*Viskositäten einer Natriumoleat-Lösung bzw.-Emulsion bei 18°.*

	Ungefroren.	2 Std. gefroren	
		bei -18°.	bei -79°.
2 Proz. Lösung	19·4 sec	19·6 sec	20·0 sec
Emulsion	20·6 sec	21·2 sec	22·0 sec

Die Erhöhung der Oberflächenspannungswerte infolge der Frostwirkung ist, verglichen mit den Werten der Eialbumin-, Gelatine- und Gummilösungen, absolut geringer; auch ist die nach der Frostwirkung eintretende Erhöhung der Oberflächenspannungswerte in allen Konzentrationen ungefähr die gleiche. Gegenüber den bei der Messung der Oberflächenspannungswerte von Eialbumin-

lösungen festgestelltem üblichen Schwankungen (Vgl. P. L e c o m t e D u N o ü y, *Equilibres superficiels des solutions colloïdales*, Paris 1929) der Messwerte sei darauf hingewiesen, dass die Messungen von Natriumoleatlösungen auch innerhalb der Fehlergrenze unveränderliche Werte liefern. Die Viskositätswerte ergeben kein einheitliches Bild. Um etwa sichtbare Unterschiede in der Veränderung der Oberfläche feststellen zu können, haben wir von den Emulsionen die mit bei  $-79^{\circ}$  gefrorenen bzw. ungefrorenen 1proz. Natriumoleatlösungen hergestellt wurden, Mikrophotogramme aufgenommen. (Abb. 5 und 6).

In Übereinstimmung mit den unwesentlichen, durch die Frostwirkung hervorgerufenen Verschiebungen der Oberflächenspannungswerte und den streuenden Viskositätswerten ist bei der von uns hier angewandten etwa 100fachen Vergrößerung eine Veränderung der Oberfläche der Emulsionsteilchen kaum festzustellen.

Ist man also geneigt, die Forderung D o n n a n s (*Z. Phys. Chem.*, 1899, **31**, 48) nach welcher in einer Emulsion sich die als Emulgator wirkende Seife in der Oberflächenschicht Öl/Wasser konzentrieren soll, auch in unseren Fällen als erfüllt anzusehen, so wird sich im Augenblick auf Grund der hier mitgeteilten Messergebnisse keine Entscheidung darüber treffen lassen, ob in der Grenzphase die Aggregate des Natriumoleats beim gefrorenen oder ungefrorenen Emulgator, oder umgekehrt, grösser oder kleiner sind.

Durch einen äusserst auffallenden Unterschied kennzeichnet sich jedoch das Verhalten auf der einen Seite der Proteine bzw. des Gummi arabicum und andererseits des Natriumoleats gegenüber insbesondere rasch einsetzender Frostwirkung. Wie aus der nachstehenden Figur eindeutig hervorgeht, weist eine z. B. bei  $-180^{\circ}$  gefrorene Natriumoleatlösung eine deutlich messbare Volumverminderung auf, wogegen der von der gefrorenen Eialbuminlösung in Reagenzglas eingenommene Raum keine mit dem Auge wahrnehmbare Veränderung zeigt (Abb. 7).

#### IV. EROETERUNG.

Um die mitgeteilten Versuchsergebnisse verstehen bzw. einer befriedigenden Erklärung zuführen zu können, müssen wir daran erinnern, dass aus den in den Tabellen (der Eialbuminlösungen) IIa–c wiedergegebenen Messungswerten klar hervorgeht, dass der Wiederanstieg der Oberflächenspannung einer gefrorenen,

verdünnten Eialbuminlösung zum Oberflächenspannungswert des Wassers absolut grösser ist als der einer gefrorenen konzentrierteren Eialbuminlösung.

Aus der Tatsache, dass sich die Oberflächenspannungen sämtlicher verdünnter kolloider Lösungen bei allen Temperaturen, bei denen ihre Kryolyse durchgeführt worden ist, beträchtlich erhöhen, wäre es zunächst naheliegend, auf Grund mancher Befunde in der Kolloidchemie die Ursache der von uns gefundenen physikalischen Veränderungen z.T. in der Dehydratation der Kolloidteilchen zu erblicken. Hieraus können wir aber die Tatsache der Anstieges der Oberflächenspannung und der gleichzeitigen Erhöhung der Gärwirkung einer gefrorenen Zymaselösung nur schwer verstehen. Es erhebt sich daher die Frage, ob nicht als Folge der Frostwirkung, unbeschadet der nicht gleichsinnigen Veränderung der Viskositätswerte einiger Lösungen, die Verkleinerung der kolloiden Teilchen und dementsprechend die Vergrößerung ihrer Oberfläche zu erörtern wäre. Daraus könnte sich nämlich ergeben, dass die absolute Annäherung des Oberflächenspannungswertes einer der Einwirkung des Frostes ausgesetzten Lösung eines lyophilen Kolloids an den Wasserwert um so grösser ist, je grösser, entsprechend der höheren Konzentration der Lösung, die neu entstandene Gesamtoberfläche der kolloiden Teilchen ist. Das Gegenteil scheint aber der Fall zu sein. Die Annäherung der Oberflächenspannungswerte der gefrorenen Lösungen eines Lyophilen Kolloids steht im umgekehrten Verhältnis zur Konzentration. Zur Erklärung dieser Erscheinung könnten wir annehmen, dass der Wert der Oberflächenspannung einer kolloiden Lösung einen Mischwert darstellt, in dem die eine Komponente aus dem Wert der Oberflächenspannung des Wassers, die andere Komponente aus der Oberflächenspannung der kolloiden Teilchen besteht.

Bevor wir auf die Folgerungen aus dieser Voraussetzung eingehen, müssen wir darauf hinweisen, dass, entsprechend unseren gegenwärtigen Vorstellungen über die Rolle des Wassers in kolloiden bzw., lebenden Systemen, in diesem Wasser selbst ein Gleichgewicht zwischen "gebundenem" Wasser und "freiem" Wasser besteht. In einer grösseren Reihe von Arbeiten ist es im Laufe des letzten Jahrzehntes der Gortnerschen Schule gelungen, diese von Gortner (R. A. Gortner, "Outlines of Biochemistry" New York, 1929, S. 230ff; *Trans. Faraday Soc.*, 1930, 26, 678), unabhängig von Balcar, Sansum und Woodyard auf-

gestellte Hypothese durch experimentelle Untersuchungen zu unterstützen, so dass wir nunmehr unter "freiem" Wasser denjenigen Teil des vorgenannten Gleichgewichtssystems verstehen könnten, der die Fähigkeit besitzt die Rolle eines Lösungsmittels zu übernehmen, wogegen das "gebundene" Wasser diese Fähigkeit verloren hat. In neuerer Zeit glaubt man (Marinero, *J. chim. Phys.*, 1931, 28, 85), sogar, den Beweis erbracht zu haben, dass, während die Dielektrizitätskonstante des "freien" Wassers 80 beträgt, diejenige des in den Kolloiden "gebundenen" Wassers auf 2-3 gesunken sein soll, und dass somit dieses "gebundene" Wasser kein Dipolmoment besitzt. Genauer genommen würde also die Oberflächenspannung einer lyophil-kolloiden Lösung durch drei Faktoren bestimmt sein, nämlich (a) durch die Oberflächenspannung des kolloiden Teilchens und (b) bzw. (c) durch die Oberflächenspannung der beiden Bestandteile des Wassersystems. Auch aus den hiesigen Befunden geht hervor, dass, verglichen mit der Oberflächenspannung einer wässrigen Lösung eines lyophilen Kolloids, der Wert der Oberflächenspannung des reinen Wassers am höchsten ist. Dieser Wert der Oberflächenspannung erniedrigt sich im Verhältnis zum Anstieg der Konzentration des Kolloids, und zwar in dem Ausmass, in dem sich das Gleichgewicht zwischen "gebundenem" und "freiem" Wasser gemäss der Konzentration der Teilchen verschoben hat. Unter der Voraussetzung, dass die Ursache des Wertanstieges der Oberflächenspannung auf einer Verkleinerung der lyophil-kolloiden Teilchen beruht, dürfte die verschiedene, absolute Erhöhung der Oberflächenspannung von Lösungen verschiedener Konzentration nunmehr leichter zu verstehen sein. Vergrössert sich nämlich unter der Frostwirkung die Oberfläche der lyophil-kolloiden Teilchen in einer konzentrierteren Lösung, so wird einerseits der Wert der Oberflächenspannung der Teilchen absolut grösser, aber gleichzeitig adsorbieren die vergrösserten Oberflächen mehr Wasser. Das Gleichgewichtsverhältnis "gebundenes" Wasser  $\rightleftharpoons$  "freies" Wasser wird zu Ungunsten der freien Komponente verschoben. Dementsprechend erhöht sich die Oberflächenspannung nur in dem Ausmass, als dies den Unterschied zwischen dem Wert der Oberflächenspannung der Teilchen und der Oberflächenspannung des Wassers entspricht. In verdünnten Lösungen sind demgegenüber weniger Teilchen vorhanden. In Übereinstimmung hiermit ist das Sinken des Oberflächenspannungswertes von reinem Wasser durch die geringere Anzahl vorhandener Teilchen bei ungefrorenen, verdünnten Lösungen geringer und die nach



der Neu-einwirkung des Frostes entstandene Oberfläche absolut kleiner. Demgemäss ist auch die zusätzlich gebundene Wassermenge geringer und der Unterschied zwischen der Oberflächenspannung der Teilchen und der Oberflächenspannung des Wassers kleiner. Dementsprechend wirkt die Teilnahme der höherwertigen Komponente (freies Wasser) dahin, dass die Erhöhung der Oberflächenspannung bei verdünnten Lösungen absolut grösser ist.

Nach diesen Ausführungen erscheint die einleitend gemachte Annahme, dass der Frost auf lyophile Kolloide *disaggregierend* und somit oberflächenvergrössernd wirkt, nicht mehr unerklärlich.

Die hiermit gleichsinnig verlaufende Erhöhung der Viskositätswerte bei den verdünnten Eialbuminlösungen befindet sich mit den vorstehenden Ausführungen in gutem Einklang; die Möglichkeit und Ursache einer nicht gleichsinnig gerichteten Veränderung der Oberflächenspannungswerte bzw. der Viskositätswerte, wie wir sie bei Gummi- und Gelatinelösungen gefunden haben, ist bereits einleitend berücksichtigt worden.

Für das Vorhandensein von gebundenem Wasser bei den kolloiden Lösungen der Eiweisskörper bzw. von Gummi arabicum spricht auch die durch Abb. 7 belegte wichtige Beobachtung, nach der die genannten Lösungen unter der Einwirkung des Frostes, im Gegensatz zu einer gefrorenen Natriumoleat-Lösung, keine sichtbaren Volumverminderungen erleiden. Es ist anzunehmen, dass unter der Einwirkung des Frostes eine Separation zwischen dem freien Wasser und dem System [kolloides Teilchen + gebundenes Wasser] stattfindet, d. h. dass das lyophile Kolloid nicht nur *irreversible* Veränderungen seiner physikalischen Eigenschaften erleidet, sondern dass das gebundene oder Hüllenwasser infolge der Kapillarkräfte, wenn überhaupt in gewöhnlichem Sinne, zweifelsohne *langsam* erfriert; d. h. der Gefrierprozess setzt bei dem freien Wasser ein. Mit anderen Worten (und dies tritt am schärfsten bei rascher Abkühlung ein) bleibt das gebundene Wasser als Adsorptionshülle bestehen, da es seine Fähigkeit, in den polaren Zustand überzugehen, eingebüsst hat. Hierdurch bleiben die Räume, die durch den Uebergang des freien Wassers in den kristallisierten Zustand entstehen, ausgefüllt, und eine Schrumpfung unterbleibt. Daraus und aus den Tatsachen, dass (a) durch das Gefrieren einer Natriumoleatlösung eine messbare Volumverminderung hervorgerufen wird, (b) andererseits, dass die Erhöhung der Oberflächenspannungswerte der gefrorenen Natriumoleatlösungen ver-

schiedener Konzentration keinen nennswerten Unterschied aufweist, (c) dass auch die absolute Erhöhung der Oberflächenspannungswerte, verglichen mit den an Eialbuminlösungen gemessenen Werten, geringer ist, und (d) das Auftauen einer Seifenlösung unter den gleichen Bedingungen unvergleichlich rascher vor sich geht als das Auftauen einer Proteinlösung, könnte der Schluss gezogen werden, dass das gebundene Wasser bei einer Seife (entsprechend auch den Tatsachen, dass die "Neutraltelchen" an ihrer Oberfläche eine ausgiebige Anzahl elektrischer Ladungen tragen bzw. im Vergleich mit dem Eialbumin das Molekulargewicht wesentlich kleiner ist) eine untergeordnetere Bedeutung hat.

In Anbetracht der Wichtigkeit, die lyophilen Kolloiden in biologischen Vorgängen zukommt, werden Schlüsse, die aus mit Seifen ausgeführten Modellversuchen auf diese Vorgänge gezogen werden, dieser Feststellung entsprechend zu werten sein. Die interessanten Beobachtungen von z. B. C l o w e s (*J. Phys. Chem.*, 1916, 20, 407) der eine Seife in der Zellwand als Emulgator annimmt, wurden aber schon früher, auch aus anderen Gründen, von S e i f r i z , (*Science*, 1923, 57, 694,) bzw. N o r d (*Protoplasma*, 1927, 2, 301) als unwahrscheinlich angesehen.

Schliesslich sei noch darauf hingewiesen, dass die Annahme, durch die Einwirkung des Frostes aus lyophile Kolloide eine i r r e v e r s i b l e physikalische Veränderung hervorgerufen zu haben, auch dadurch berechtigt erscheint, dass durch wiederholtes Frieren praktisch keinerlei Unterschiede in den Viskositäts- bzw. Oberflächenspannungswerten festgestellt werden konnte.

#### V. EINFLUSS DER FROSTWIRKUNG AUF DIE LEITFÄHIGKEIT UND KATAPHORETISCHE WANDERUNGSGESCHWINDIGKEIT.

In den oben mitgeteilten Versuchen bzw. deren Erörterung glauben wir, die früher aufgestellte Hypothese, nach der die Veränderung der Oberflächenspannung bzw. der Viskosität einer der Frostwirkung ausgesetzten lyophil-kolloiden Lösung auf die Disaggregation-Aggregation ihrer Teilchen zurückzuführen ist, weiter gestützt zu haben. Folgerichtig ist hieraus bei Enzymlösungen, die sich gleichfalls als Lösungen verdünnter lyophiler Kolloide verhalten, sich aber nach eingetretener Frostwirkung vorübergehend als höher wirksam, insgesamt aber als dauernder wirksam erwiesen haben, angenommen worden, dass die unter dem Einfluss der Frostwirkung neu

entstandene kombinierte Träger-Enzymoberfläche dem Einfluss z. B. der Proteolyse oder Zellstoffwechselprodukten gegenüber, empfindlicher ist, aber durch Adsorption z. B. von Gasen geschützt werden kann (Protektorwirkung). Die experimentelle Bestätigung hierfür ist in einer unserer früheren Mitteilungen niedergelegt worden.

Um die experimentellen Grundlagen unserer Auffassung zu verdichten, war es naheliegend, sowohl die Leitfähigkeit der Frostwirkung ausgesetzter lyophiler kolloider Lösungen bzw. Emulsionen als auch die kataphoretische Wanderungsgeschwindigkeit lyophilkolloider Teilchen im elektrischen Felde zu messen.

TABELLE XII.

*Spezifische Leitfähigkeiten von gefrorenen und ungefrorenen Eialbumin, Gelatine-\*, Gummiarabicum- und Natriumoleatlösungen, b. 22°.*

Konzentration der Lösung.	Ungefroren.	Gefroren			
		2 Stden b. +18°.	48 Stden b. -18°.	2 Stden b. -79°.	2 Stden b. -180°.
Eialbumin 0.01%	$1.103 \times 10^{-5}$	$1.480 \times 10^{-5}$	$1.863 \times 10^{-5}$	$1.125 \times 10^{-5}$	$1.125 \times 10^{-5}$
Eialbumin 0.1%	$1.110 \times 10^{-4}$	$1.016 \times 10^{-4}$	$1.110 \times 10^{-4}$	$8.589 \times 10^{-5}$	$8.589 \times 10^{-5}$
Gelatine 0.5%	$8.192 \times 10^{-5}$	—	$8.192 \times 10^{-5}$	—	$7.946 \times 10^{-5}$
Gummi 0.01%	$1.081 \times 10^{-5}$	—	$4.307 \times 10^{-5}$	$1.182 \times 10^{-5}$	$1.182 \times 10^{-5}$
Gummi 0.1%	$2.681 \times 10^{-5}$	—	—	$2.381 \times 10^{-5}$	$2.381 \times 10^{-5}$
Natriumoleat 0.001%	$9.609 \times 10^{-6}$	$1.058 \times 10^{-5}$	$7.403 \times 10^{-5}$	—	$7.403 \times 10^{-5}$
Natriumoleat 0.1%	$1.699 \times 10^{-4}$	—	$1.122 \times 10^{-4}$	$1.122 \times 10^{-4}$	$1.122 \times 10^{-4}$

TABELLE XIII.

*Spezifische Leitfähigkeit von gefrorenen und ungefrorenen 2proz. Eialbumin-, Gummi arabicum-, Saponin-, Natriumoleatlösungen bzw. den damit hergestellten Emulsionen bei 18°.*

	Ungefroren.	2 Std. gefroren	
		bei -18°.	bei -79°.
Eialbumin	$1.977 \times 10^{-3}$	$2.000 \times 10^{-3}$	$2.142 \times 10^{-3}$
Emulsion	$1.191 \times 10^{-3}$	$1.989 \times 10^{-3}$	$2.102 \times 10^{-3}$
Gummi arabicum	$3.484 \times 10^{-4}$	$3.424 \times 10^{-4}$	$3.208 \times 10^{-4}$
Emulsion	$3.444 \times 10^{-4}$	$3.362 \times 10^{-4}$	$3.405 \times 10^{-4}$
Saponin	$5.795 \times 10^{-4}$	$5.370 \times 10^{-4}$	$5.641 \times 10^{-4}$
Emulsion	$5.793 \times 10^{-4}$	$5.672 \times 10^{-4}$	$5.492 \times 10^{-4}$
Natriumoleat	$1.360 \times 10^{-3}$	$1.310 \times 10^{-3}$	$1.245 \times 10^{-3}$
Emulsion	$1.066 \times 10^{-3}$	$1.068 \times 10^{-3}$	$9.845 \times 10^{-4}$

\* Gelatinelösungen geringerer Konzentration waren mit unserer Apparatur nicht zu messen.

Aus den Tabellen geht hervor, dass in Uebereinstimmung mit dem Einfluss der Konzentration die verdünnten Lösungen nach dem Frieren bei allen Temperaturen ein Ansteigen der Leitfähigkeit, wogegen konzentriertere Lösungen ein Sinken der Leitfähigkeit mit Ausnahme von Eialbumin, verglichen mit der Leitfähigkeit der ungefrorenen Lösungen, aufweisen. Nur eine scheinbare Ausnahme ist bei der Betrachtung der Ergebnisse der Leitfähigkeitsmessungen an 2% igen Eialbumin-Lösungen nach Einwirkung des Frostes bzw. an mit gefroren gewesenem Eialbumin hergestellten Emulsionen zu beobachten. Sie erklärt sich aber zwanglos angesichts unserer auf S. 4 gemachten Ausführungen. Diesen entsprechend haben wir es in dieser Konzentration vorwiegend mit einer wahrscheinlich bis zur Koagulation fortschreitenden Aggregation zu tun. Die gestiegene Leitfähigkeit ergibt sich dann hauptsächlich aus der der disaggregierten Teilchen.

TABELLE XIV.

*Kataphoretische Wanderungsgeschwindigkeit gefrorener und ungefrorener Eiweiss- und Gelatinelösungen bei 19°.*

Lösung.	Einflusszeit in Minuten.	Messdauer in Minuten.	Wanderung in mm.
Eiweiss 1% Ungefr.	75	145	3·2 Kathodische Wanderung
Eiweiss 1%, 4 Stden bei -18° gefroren	90	145	6·9 Kathodische Wanderung
Eiweiss 0·2% Ungefr.	80	150	1·8 Kathodische Wanderung
Eiweiss 0·2% 4 Stden b. -18° gefroren	80	123	3·0 Kathodische Wanderung
Gelatine 0·5% Ungefr.	120	115	4·8 Kathodische Wanderung
Gelatine 0·5%, 4 Stden b. -18° gefroren	90	100	6·0 Kathodische Wanderung

Bei Betrachtung der in der Tabelle XIV wiedergegebenen Messwerte ergibt sich, dass die kataphoretische Wanderungsgeschwindigkeit der Teilchen der gemessenen lyophil-kolloiden Lösungen nach dem Frieren ungefähr auf das Doppelte gestiegen ist. Die kataphoretische Wanderungsgeschwindigkeit der Gelatinelösungen ist absolut grösser als die der Eialbuminlösungen.

## VI. EROERTERUNGEN.

Die hier mitgeteilten Befunde stehen in vollem Einklang mit den bekannten Untersuchungsergebnissen von Mc Bain und seinen Mitarbeitern (Vgl. Mc Bain, Laing und Titley, *J. Chem. Soc.*, 1919, 118, 1279) denen die starke Leitfähigkeit von Seifenlösungen sich umgekehrt zu den Veränderungen der Konzentrationen und der Temperatur verhält. An Stelle der gewöhnlichen Fettsäureanionen treten nämlich als Mizellen rasch wandernde Anionen auf, insbesondere bei den höheren und bei grösseren Konzentrationen. Aber auch in der konzentrierten Lösung bildet lediglich der auf die Kolloide entfallende Teil der Leitfähigkeit den grösseren Teil der Gesamtleitfähigkeit. Eine gute Bestätigung der Annahme von der disaggregierenden und somit oberflächenvergrössernden Wirkung des Frostes liegt schliesslich in der Tatsache, dass die Leitfähigkeit der verdünnteren Lösungen stark zugenommen hat. Wir wissen ja aus den Untersuchungen von Nordenson (*Kolloid Z.*, 1915, 16, 65) dass die Leitfähigkeit von dispersen Systemen, die die gleiche Stoffmenge in verschiedener disperser Verteilung enthalten, sich umgekehrt verhalten wie die Quadrate der Teilchenradien. Die Leitfähigkeit selbst rührt von den höchst dispersen Teilen des Kolloids her.

Die von uns erhaltenen Messergebnisse bei Protein- und Gummi arabicum-Lösungen stehen in Einklang mit den an Seifenlösungen erhaltenen Befunden.

Schliesslich könnte unsere Auffassung von der Vergrösserung der Oberfläche der Kolloidteilchen als erhärtet angesehen werden durch die Ergebnisse der Messungen der kataphoretischen Wanderungsgeschwindigkeit. Es kann angenommen werden, dass infolge der Verteilung Elektrolyte aus den Proteinen in Lösung gegangen sind. Dadurch fand eine elektrische Aufladung der Teilchen statt, wodurch die kataphoretische Wanderungsgeschwindigkeit sich erhöht hat.

## VII. MATHEMATISCHE AUSWERTUNG.

Im Folgenden wurde noch der Versuch unternommen, die Anwendbarkeit der Gleichungen von v. Smoluchowski (*Kolloid Z.*, 1916, 18, 194) bzw. Einstein (*Ann. Physik*, 1906, iv, 19, 289) bei unseren theoretischen Ueberlegungen auf Grund einiger Versuchsdaten zu prüfen,

Die Viskosität wird in der Gleichung von v. Smoluchowski, wie folgt, ausgedrückt:

$$\eta_s = \eta_m \left\{ 1 + K\phi \left[ 1 + \frac{1}{\lambda \eta_m r^2} \left( \frac{D\xi}{2\pi} \right)^2 \right] \right\}$$

Hier bedeuten  $\eta_s$  = die Viskosität der kolloiden Lösung,  $\eta_m$  = die der reinen Flüssigkeit,  $\phi$  = das Volumen der Teilchen in der Volumeneinheit der kolloiden Lösung,  $\lambda$  = die spec. Leitfähigkeit,  $r$  = den Radius der Teilchen,  $D$  = die Dielektrizitätskonstante,  $\xi$  = den electrokinetischen Potentialsprung,  $K$  = eine Konstante.

Mit Ausnahme der Grösse der Teilchenradien können sämtliche für die Auswertung der Gleichung erforderlichen Daten aus der hiesigen Untersuchung entnommen werden. Der Radius des Eiweissmoleküls  $2.18 \mu\mu$  ist der Arbeit von Svedberg und Sjögren (*loc. cit.*) entnommen. Dagegen wurde der Radius der Gelatineteilchen mit Hilfe der Angaben von Krishnamurti und Svedberg (*J. Amer. Chem. Soc.*, 1930, **52**, 2897), auf Grund eines spezifischen Volumens  $= 0.692$  und des für die hiesigen Berechnungen ungünstigsten Molekulargewichts  $= 10000$  ermittelt. Auf dieser Grundlage ergibt sich der Wert von  $1.40 \mu\mu$  für den Radius des Gelatinemoleküls. Da der Angabe für die kataphoretische Wanderungsgeschwindigkeit der Eialbuminteilchen Messungen an einer 0.1 proz. Lösung zugrunde gelegt sind, konnte um so eher vorausgesetzt werden, dass sie mit der kataphoretischen Wanderungsgeschwindigkeit einer 0.5 proz. Lösung übereinstimmt. Es wurde auch angenommen, dass kein Unterschied bei der kataphoretischen Wanderungsgeschwindigkeit bei  $19^\circ$  und  $22^\circ$  besteht. Nach der von Herrn Dr. H. B. Bull\* vorgenommenen Umwandlung unserer Daten in die erforderlichen Einheiten ergibt sich, dass der die elektrischen Veränderungen betreffende Teil der Gleichung

$$\frac{1}{\lambda \eta_m r^2} \left( \frac{D\xi}{2\pi} \right)^2$$

im Falle des Eialbumins  $= 2.15 \times 10^{-3}$  und im Falle der Gelatine  $5.45 \times 10^{-3}$  beträgt. Beide Zahlen sind wesentlich kleiner als 1

\* Fellow des National Research Council, U. S. A.

und können daher vernachlässigt werden, wodurch lediglich der von E i n s t e i n begründete Teil der Gleichung

$$\eta_s = \eta_M (1 + K\phi)$$

zur Geltung kommt. Obwohl diese Gleichung nicht immer geeignet ist, quantitative Aussagen zu ermöglichen, ist sie ohne weiteres für die Unterstützung qualitativer Zwecke verwendbar. Im Sinne der E i n s t e i n schen Gleichung bedeuten daher unsere Befunde, dass im Falle des Eialbumins eine Vergrößerung des Gesamtvolumens der suspendierten Teilchen und im Falle der Gelatine eine Verringerung unter Einwirkung desselben physikalischen Einflusses eingetreten ist. Beide Befunde erhärten die Auffassung, dass infolge der Frostwirkung beim Eialbumin eine irreversible Vergrößerung der Oberfläche der Teilchen unter Vermehrung des "gebundenen" Wassers eintritt, und im Falle der Gelatine eine Disaggregation-Aggregation der Teilchen stattfindet, bei der das Verhältnis zu Gunsten der letzteren verschoben ist.

#### VIII. ZUSAMMENFASSUNG.

Ausgangspunkt unserer Untersuchungen war die Beobachtung, dass eine lyophil-kolloide Zymaselösung, nachdem sie der Frostwirkung ausgesetzt und wieder aufgetaut war, unter sonst gleichgebliebenen Versuchsbedingungen eine vorübergehend erhöhte Wirksamkeit zu entfalten vermag. Es wurde aus der nur vorübergehend erhöhten Wirksamkeit der Schluss gezogen, dass unter der Einwirkung des Frostes eine Vergrößerung der Oberfläche eintritt, die wiederum eine Steigerung der Empfindlichkeit gegen intermediäre Vorgänge bzw. Reaktionsprodukte nach sich zieht. Nachdem wir noch vorher den Nachweis erbracht und als a l l g e m e i n g ü l t i g angesprochen haben, dass gasformige und andere Verbindungen die Steigerung der enzymatischen Tätigkeit in verschiedenen Zellsystemen durch Erhöhung der Zellpermeabilität bewirken, haben wir nachher experimentell belegt, dass dieselben Verbindungen durch lyophil-kolloide Teilchen verzehrt werden und somit eine P r o t e k t o r w i r k u n g ausüben können. Hieraus ergibt sich mit Gewissheit, dass unsere Adsorptive in biologisch wichtigen Reaktionen eine zweifache Rolle zu spielen vermögen.

In der gegenwärtigen Untersuchung konnte dann mit Hilfe der Kryolyse und nachfolgender Messung der oberflächenspannung, Tropfenzahl, Viskosität, elektrischen Leitfähigkeit bzw. kataphoretische Wanderungsgeschwindigkeit der Nachweis erbracht werden, dass die lyophilen Kolloide unter dem Einfluss des Frostes sowohl in Lösungen als auch bei Emulsionen eine irreversible physikalische Veränderung erleiden. Bei sämtlichen im verdünnten Bereich vorgenommenen Messungen war bei allen Kolloiden die Richtung der Veränderung gleichsinnig,—eine übereinstimmende, wenn auch nicht gleichsinnige Veränderung bei sämtlichen Messungen an den konzentrierten Lösungen bzw. Emulsionen konnte nur im Falle des Eialbumins beobachtet werden. Die Beständigkeit der mit gefrorenen gewesenen Emulgatoren hergestellten Emulsionen zeigte eine leichte Steigerung gegenüber Emulsionen, die mit ungefrorenen Emulgatoren hergestellt waren.

Da Eiweiss nach dem derzeitigen Stand unserer Kenntnisse nicht nur als Substanz für krystallisierte Enzyme in Frage kommt, sondern auch für die Eigenschaften der sogenannten Trägersubstanzen verantwortlich ist, so können diese Befunde als weiterer exakter Beweis der Abhängigkeit der Funktionen eines kolloiden Trägers von seinem physikalischen Zustand, z. B. dem Dispersitätsgrad angesehen werden.

Die Untersuchung erfreute sich der dankenswerten Förderung der Notgemeinschaft der Deutschen Wissenschaft.





NORD

ABB. 1.

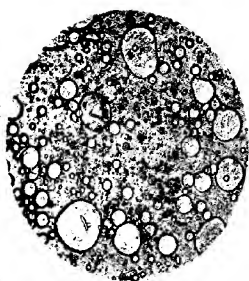


ABB. 2.

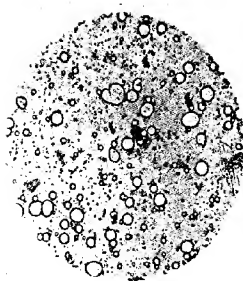


ABB. 3.

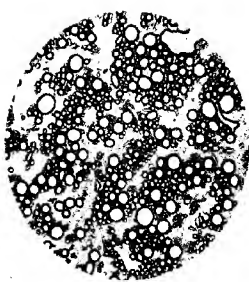
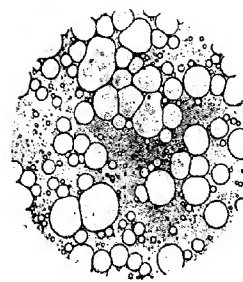


ABB. 4.





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ABB. 5.

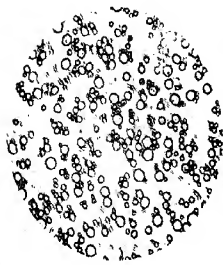


ABB. 6.

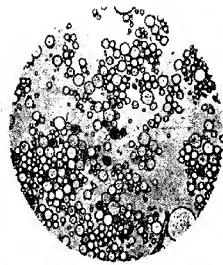


ABB. 7.



Reagenzgläser, enthaltend die gleiche Menge je einer 0.1% b. -180° gefrorenen  
Eialbumin—(rechts) bzw. Natriumoleatlösung (links) in  
gefrorenen Zustand.



## Synthesis of Anthraquinones Occurring in Nature.

By P. C. MITTER.

The problem of synthesis of anthraquinones occurring in nature reduces itself ultimately to the synthesis of hydroxyanthraquinones or hydroxymethylantraquinones or their *O*-methyl ethers with the substituting groups in certain definite positions. Some of these contain a carboxyl group in place of the methyl group while only in one case namely that of aloe-emodin, a carbinol group has been found to occur.

The naturally occurring anthraquinones may be classified into four distinct types. In two of these namely chay-root and madder types all the substituents occur in one benzene ring while in the other two namely morindone and emodin types, the substituents occur in both the benzene rings. The distribution of substituents in all the four types appears to obey the following empirical laws:

(1) No naturally occurring anthraquinone derivative contains more than four substituents in the two benzene nuclei namely, not more than one methyl (or carboxyl or carbinol) group which, if present, always occupies a  $\beta$ -position, and not more than three hydroxyl (or methoxyl) groups.

(2) The substances containing the maximum number of substituents constitute the fundamental types and the other anthraquinone derivatives occurring in the same plant are all derived from the fundamental types by a permutation or combination of the groups, at least one  $\beta$ -standing group being present.

(3) Of the four substituents two (including the methyl or carboxyl or carbinol group, if present) occupy  $\beta$ -positions and the other two occupy  $\alpha$ -positions.

(4) If both the  $\beta$ -substituents are in one ring the other substituents also occur in the same ring or, in other words, a homonuclear type is formed. If both the  $\beta$ -substituents are hydroxyl groups they must occur in the same ring.

(5) If the  $\beta$ -substituents are in different rings the  $\alpha$ -substituents are distributed in such a way as to produce a symmetrical configuration.

*Type I: Chay-root Type.*

Our knowledge of this group is derived mainly from the researches of A. G. Perkin and his co-workers (*J. Chem. Soc.*, 1893, **63**, 1160; 1895, **67**, 817). The substances present in chay-root include 2-oxyanthraquinone, alizarin, alizarin-1-*O*-methyl ether, anthragallol-1:3-dimethyl ether, anthragallol-1:2-dimethyl ether and hystazarin monomethyl ether.

Their syntheses have been achieved mainly by the condensation of phthalic anhydride with the corresponding phenol or phenol ether followed by methylation or demethylation, complete or partial. It is interesting to note that in this, as in other groups of anthraquinones occurring in nature the  $\alpha$ -methyl ethers predominate. Perkin and Storey (*J. Chem. Soc.*, 1928, 229) have worked out a general method for the synthesis of such ethers.

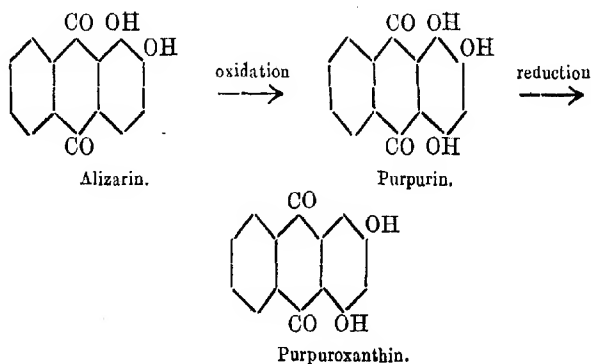
*Type II: Madder Type.*

The anthraquinones of the madder type fall into two sub-groups:

(i) Those containing OH groups only like alizarin, purpurin and purpuroxanthin.

(ii) Those containing in addition methyl or carboxyl groups like rubiadin, rubiadin- $\alpha$ -methyl ether, munjisthin and pseudopurpurin.

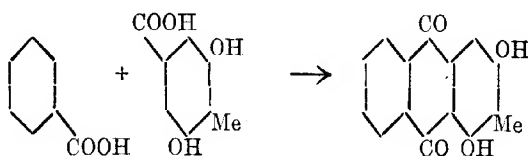
The method of synthesis of alizarin is too well known to be repeated here. Alizarin gives purpurin on oxidation with manganese dioxide and sulphuric acid (De Lalande, *Jahresb. der Chemie*, 1874, p. 486), while the latter gives on reduction purpuroxanthin (Liebermann, *Annalen*, 1876, **183**, 214).



All the members of the sub-group are thus interrelated.

Purpuroxanthin can also be synthesised by condensing 3: 6-dihydroxybenzoic acid with benzoic acid (Noah, *Annalen*, 1887, 240, 266).

Of the members of the second sub-group, rubiadin was first synthesised by Mitter and Gupta by condensing 2:6-dihydroxy-*p*-toluic acid with benzoic acid (*J. Indian Chem. Soc.*, 1928, 5, 25).



Rubiadin.

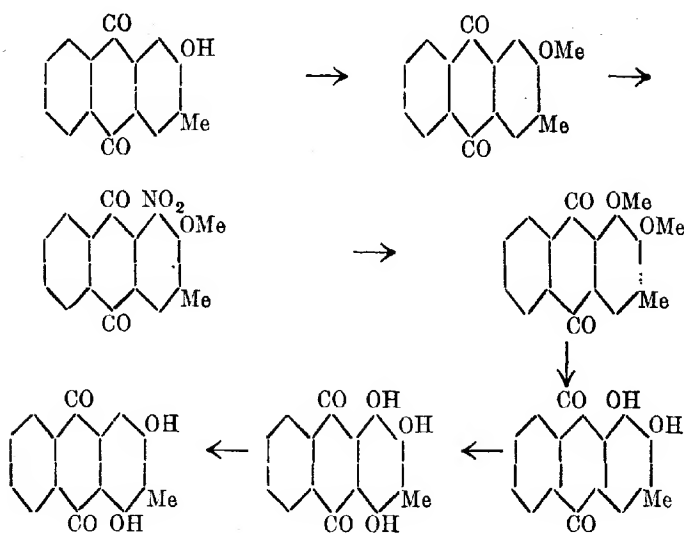
It was also synthesised by condensing 2: 6-dimethoxytoluene with phthalic anhydride followed by subsequent ring-closing and demethylation (Mitter and Biswas, *J. Indian Chem. Soc.*, 1930, 7, 839), while rubiadin-1-*O*-methyl ether was synthesised by Jones and Robertson (*J. Chem. Soc.*, 1930, 1706) by methylating 3-*O*-acetyl-rubiadin with methyl iodide and silver oxide and deacetylating the product.

Another method of rubiadin synthesis devised by Mitter and Pal (*J. Indian Chem. Soc.*, 1930, 7, 260) was found to be capable of considerable extension. The starting point in this synthesis was 2-hydroxy-3-methylantraquinone, a substance which was first prepared in a very impure form by Froude (*Annalen*, 1880, 202, 165). Mitter and Sen (*J. Indian Chem. Soc.*, 1928, 5, 634) could obtain the substance in a pure state and they also proved that Froude's substance was really a mixture of 1-hydroxy-2-methyl-, 1-methyl-2-hydroxy-, and 2-hydroxy-3-methylantraquinones. The last named substance could be converted into rubiadin according to the following scheme:

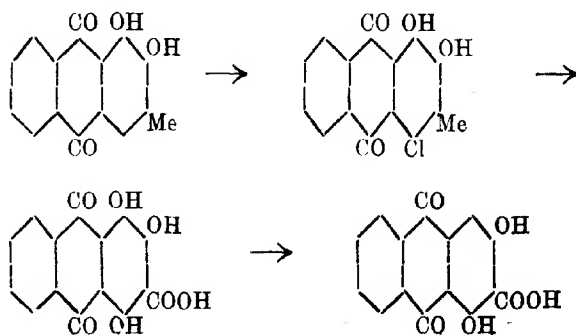
It was first methylated with dimethyl sulphate and alkali and then nitrated by treatment with potassium nitrate in presence of sulphuric acid, when 1-nitro-2-methoxy-3-methylantraquinone was obtained. On digestion with potassium methoxide in methyl alcoholic solution, this gave the dimethyl ether of 3-methylalizarin, which was demethylated and then oxidised with manganese dioxide



and sulphuric acid to 3-methylpurpurin. On reduction with stannous chloride in alkaline solution, this gave rubiadin.



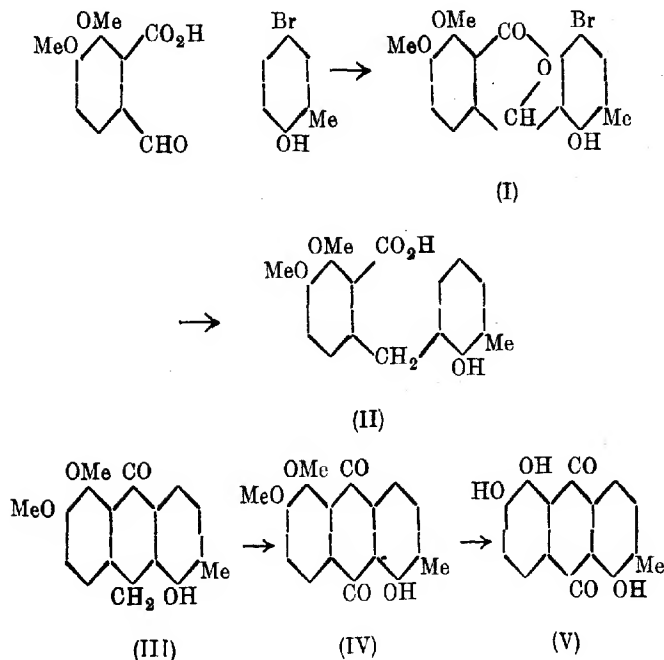
The method was subsequently extended by Mitter and Biswas for the synthesis of munjisthin (*Ber.*, 1932, **68**, 622). Chlorination of 3-methylalizarin with sulphuryl chloride in nitrobenzene gave 1:2-dihydroxy-3-methyl-4-chloroanthraquinone, which on oxidation with nitrous acid in presence of boric and sulphuric acids gave pseudopurpurin. On reduction with sodium hydrosulphite and ammonia at 15°, according to method of D.R.P. 212697 munjisthin is obtained.



It may be noted here that pseudopurpurin had been previously synthesised by the oxidation of alizarin-3-carboxylic acid with manganese dioxide and sulphuric acid (D.R.P. 260765).

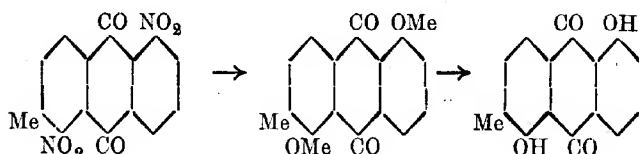
*Type III: Morindone Type.*

A new synthetic method was developed by Jacobson and Adams (*J. Amer. Chem. Soc.*, 1924, **46**, 2788) for the synthesis of morindone. They condensed ophanic acid with *p*-bromo-*o*-cresol with the help of 35% sulphuric acid and converted the phthalide (I) thus obtained by reduction with zinc and 10% sodium hydroxide into the corresponding phenyltolylmethane carboxylic acid (II). On ring-closing this gave the anthrone (III) which on oxidation with chromic acid in glacial acetic acid gave a dimethyl ether of morindone (IV) from which morindone (V) was obtained by demethylation.

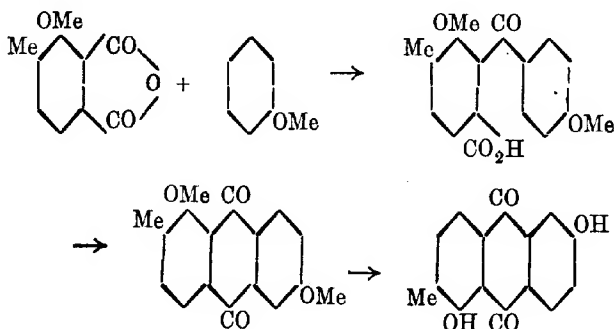


Two other anthraquinones of the morindone type are known namely, morindadiol and soranjidiol. The former was isolated by Oesterle and Tisza (*Arch. Pharm.*, 1908, **246**, 150) from *Morinda citrifolia*. Mitter and Biswas (*J. Indian Chem. Soc.*, 1928, **5**, 769)

hold that the substance is probably identical with 1:5-dihydroxy-6-methylantraquinone which they obtained from 1:5-dinitro-6-methylantraquinone (Eder, Widmer and Büttler, *Helv. Chim. Acta*, 1924, 7, 341) by converting the substance into the corresponding dimethoxyantraquinone by the method of Kaufler (*Ber.*, 1904, 37, 65) and demethylating the product.



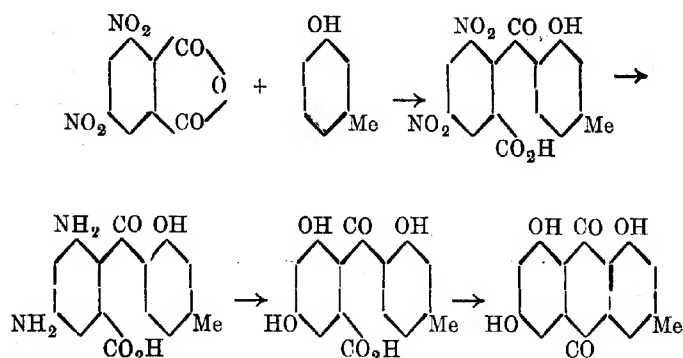
They have also shown (*loc. cit.*) that soranjidiol, which was also isolated by Oesterle and Tisza (*loc. cit.*) is most probably identical with the dihydroxymethylantraquinone isolated by Perkin and Hummel (*J. Chem. Soc.*, 1894, 65, 851) from Mangkoudu, the root-bark of *Morinda umbellata*. Its properties agree very closely with that of 2:5-dihydroxy-6-methylantraquinone prepared by Simonsen and Rau (*J. Chem. Soc.*, 1921, 119, 1340) by condensing 3-methoxy-4-methylphthalic anhydride with anisol, followed by ring-closing and demethylation.



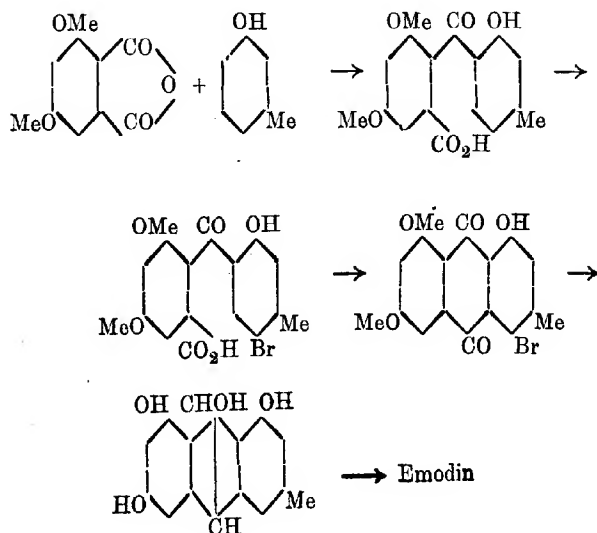
*Type IV: Emodin Type.*

Eder and Widmer (*Helv. Chim. Acta*, 1922, 5, 3) obtained chrysophanic acid by condensing 3-nitrophthalic anhydride with *m*-cresol, conversion of the nitrobenzoylbenzoic acid by reduction, followed by diazotisation into the corresponding hydroxybenzoylbenzoic acid and subsequent ring-closing. A similar method has been adopted by

the same authors (*Helv. Chim. Acta*, 1923, **6**, 966) for the synthesis of emodin, the starting materials being 3:5-dinitrophthalic anhydride and *m*-cresol.

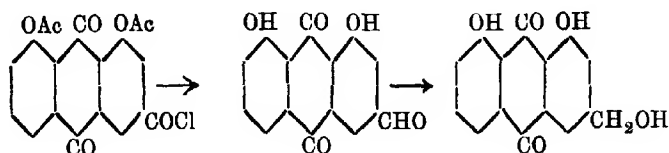


In their synthesis of emodin, Jacobson and Adams (*J. Amer. Chem. Soc.*, 1924, **46**, 1312) condense 3:5-dimethoxyphthalic anhydride with *m*-cresol and convert the benzoylbenzoic acid so obtained into its bromo derivative which is submitted to ring-closing. Reduction with hydriodic acid gives rise to the anthranol from which on oxidation with chromic acid in glacial acetic acid, emodin is obtained.



As chrysophanic acid can be converted by oxidation into rhein (Oesterle, *Schweizer. Wochens. f. Chemie u. Pharmazie*, 1903, No. 50), the synthesis of the former implies also the synthesis of the latter.

Mitter and Banerjee (*J. Indian Chem. Soc.*, 1932, 9, 875) have synthesised aloë-emodin by converting diacetylrhein chloride into 1:8-dihydroxyanthraquinone-3-aldehyde, by reduction with hydrogen in presence of palladiumised barium sulphate (Rosenmund, *Ber.*, 1918, 51, 585 ; 1921, 54, 425). On further reduction with hydrogen in presence of platinum oxide with ferrous chloride as promoter according to the method of Roger Adams and his co-workers (*J. Amer. Chem. Soc.*, 1922, 44, 1397 ; 1923, 45, 1071, 2171 ; 1924, 46, 1675) the aldehyde is converted into aloë-emodin.



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## Spectroscopy in the Service of Chemistry.

By M. N. САПА.

### *Introduction.*

There was a tendency, amongst the philosophers of early times, to deduce every problem with which mankind comes across, regarding life and nature, from a First Principle, or from a small number of simple principles. Experience of centuries showed the futility of such attempts. Nature is *diverse* and every one of her phenomena must be studied separately. So it happened that when scientific studies of nature were revived in Europe, contemporaneously with the French Revolution, every branch of science began to be studied by itself. Thus modern chemistry, the different branches of physics, the biological sciences were all studied and developed in separate closed compartments. The result of such intensive studies was a rich harvest of profound discoveries of facts and phenomena in each branch of science, which revealed the unsuspected diversity of natural phenomena. But the human mind refuses to believe in complexity and before long, active minds were busy in finding out whether some unifying principles do not exist beneath the superstratum of all these apparent diversities. The formulation of the atomic theory, the discovery of the electromagnetic theory of light, the modern theories of electrical structure of matter are the fruitful results of such enquiries.

The connection between the phenomena of light, and chemical phenomena has been long suspected. Sir P. C. Rây, in his monumental History of Hindu Chemistry quotes from a iatro-chemical treatise of the eighth century how the ancient Indian savants could find out the elements occurring in an ore from the coloration which they imparted to flames.

"Copper yields a blue flame.....that of tin is pigeon coloured.....that of lead is pale tinted.....that of iron is tawny.....that of "peacock ore is red." [Rasaratna Samuchhaya, History of Hindu Chemistry, Vol. I. p. 38.]

No notice was taken of this observation for twelve hundred years, but it is well-known that seventy years ago, a scientific investigation

of this fact of observation led Kirchoff to the great discovery of Spectrum Analysis. Kirchoff and Bunsen, and other chemists and physicists like L. de Boisbourdan, Urbain, Lockyer, Nielson and Ramsay were quick to grasp the great importance of this discovery, and seek for new elements in minerals, as well as in heavenly bodies. To-day not less than 40 elements out of a total of 92 stand to the credit of spectrum analysis.

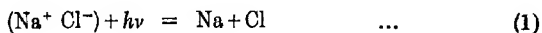
For a long time it appeared that excepting its application to discovery of new elements, spectroscopy would not have much use for the chemist, and would not help him in the solution of such problems as those of valency, origin of chemical forces, explanation of photochemical actions, characteristic colours shown by organic or inorganic salts. Recent events have however shown that such is not the case. The previous attitude prevailed for a long time because the chemist and the physicist had a dread for the complexity of spectral data. An element like Fe gives no less than 6000 lines in the visible region and to report the whole information regarding the spectra of atoms alone, even eight bulky volumes of Kayser and Runge have not been found sufficient. The spectra of molecules with which the chemist is more concerned are still further diverse and complex. Hence it is not a matter of surprise that the chemist would find it extremely difficult to make any use of spectroscopy, and would look upon such attempts with horror and dismay.

But in recent times, thanks to the recent developments in physics, the situation has entirely changed. Due to the discovery of the quantum theory of radiation, the development of the nuclear theory of atoms, and the theories of spectra of atoms, it has been found possible to reduce the whole mass of data in the spectra of atoms to a few simple rules. The application of the new theories to explanation of the problems facing the chemist has also been started and it has already yielded such fine results that it is hoped that in a short time, *a student of chemistry will find a knowledge of modern theories of spectroscopy as valuable as the knowledge of the different methods of group analysis.* It is impossible to give a complete account of all the attempts, but I shall try to indicate a few lines in which very fruitful results have been achieved.

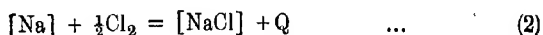
#### *On the Nature of Chemical Forces.*

The nature of the forces which bind two or more atoms to give rise to the molecules which are ordinarily met with have taxed the

ingenuity of chemists and physicists for a long time. Since the times of Berzelius the forces in compounds of the type NaCl have been thought to be of electrical origin. It is supposed that when an atom like Na which contains one electron which it can easily lose, and another like Cl which shows an affinity for an electron, come together, the valency electron leaves Na and goes over to Cl. Thus the molecule really consists of  $(\text{Na}^+, \text{Cl}^-)$ . The forces of binding are therefore of electrostatic origin. Such compounds are known as polar or ionic compounds. This hypothesis has been put on a scientific foundation by the spectroscopic work of Franck and his students. They have shown that the absorption spectra of these compounds are continuous, beginning from a long wave-length limit. Franck interprets this result in the following way:—When a quantum of energy  $h\nu$  falls on a molecule, it acts on an electron, and raises it to a higher orbit (if such an orbit exists) or removes it altogether from the anion to the cation. In the present case,  $\text{Cl}^-$  ion has the most loosely bound electron, and this has no further stable orbit. So provided the incident light has the proper energy, it detaches itself completely from  $\text{Cl}^-$  and attaches to  $\text{Na}^+$ . So the absorption limit  $\nu_1$ , corresponds to the process



If this theory be correct,  $h\nu$  should be equivalent to the energy of formation of NaCl vapour out of gaseous Na and Cl atoms. In thermochemistry, the heat of formation is usually determined by taking the substances in the forms in which they are usually available. Thus we have



where  $[\text{Na}]$  denotes sodium in the solid state,  $\text{Cl}_2$  denotes a chlorine molecule, and  $Q$  is the heat of formation. From this the atomic heat of formation, defined by the relation



is obtained with the aid of the thermochemical relationship

$$R = Q + L_{\text{Na}} + \frac{1}{2}D_{\text{Cl}_2} - L_{\text{NaCl}} \quad \dots$$



Calculation shows that  $R=118$  Cal for NaCl;  $L_{Na}$ =latent heat of evaporation of Na;  $L_{NaCl}$ =latent heat of NaCl. The value of  $\lambda_0$ , the beginning of absorption can be calculated from the relation

$$\lambda_0 = \frac{286000}{R \text{ in Cal}} \quad \dots \quad \dots \quad (5)$$

For NaCl,  $\lambda_0$  was found to be  $2428 \text{ \AA}$  which corresponds to  $R=118$  Cal. The agreement is therefore very satisfactory. Similar agreement has been found in the case of all the alkali halides.

#### *Excitation of Higher States.*

Further proof of the essential correctness of Franck's hypothesis is afforded by the idea that the electron from Cl may separate from it in such a way that the Cl atom is left not in the normal Cl ( $^2P_{3/2}$ -state) but in the metastable Cl ( $^2P_{1/2}$ -state).

If  $\nu_2$  is the beginning of absorption in the second process it is found that this beginning is shifted according to the following relation

$$\nu_2 = \nu_1 + ({}^2P_{3/2} - {}^2P_{1/2}) \text{ of the halogen atom} \quad \dots \quad (6)$$

For Cl, Br and I atoms, the  ${}^2P_{3/2} - {}^2P_{1/2}$  values are 880, 3700, and 7600 respectively. Hence the absorption curves for the two kinds of splitting will be very close to each other for Cl but should be separable for Br and I. Actually the absorption curves for bromides and iodides show two maxima, which are roughly separated by the  $({}^2P_{3/2} - {}^2P_{1/2})$ -separations. This affords a further confirmation of Franck's theory. So as regards the alkali halides, the correctness of Franck's hypothesis seems to be well established.

#### *Origin of Chemical Forces in Homopolar Compounds.*

But there are a certain class of compounds like  $H_2$ ,  $I_2$ ,  $ICl$ ..... where the attraction between constituent atoms cannot be of electrical origin. For example in  $H_2$ , we cannot conceive that one constituent is  $H^+$ , the other is  $H^-$ . The constituents must be H and H. What is the origin of chemical forces of attraction in such a case? Both constituents are electrically neutral, hence the force of attraction must arise from some other cause. The discovery of the origin of

this force is due to Heitler and London.<sup>2</sup> They showed that the force arises from the resonance interaction of the electrons in each atom. As the expression stands, it is probably unintelligible to the majority of chemists, but it becomes clear when we bear in mind the fruitful discovery, that the electron is not merely a point charge of electricity, but is also a magneton, *i.e.*, electrons possess magnetic moment of definite values. Thus though the two H-atoms exert no attractive force of electrical origin on each other, the electrons in each, according to Pauli's principle, have their magnetic axis in opposite directions, and so attract each other. This is probably not quite a correct description of the Heitler-London force, but this may serve to convey some idea of it. When the electrons have their spin axes in the opposite directions, they form a state known as  $^1\Sigma_1$ ; when they are in the same directions, they form the state  $^3\Sigma$ . Heitler and London showed that in the first state, the potential energy of two atoms runs through a minimum as the distance between them varies while in the second case, it continuously diminishes with increasing distance. The first state is therefore one of stable equilibrium giving us the normal H atom, while the second is an unstable configuration. The energy of this H atom as calculated from quantum mechanics by Wang and others, exactly agrees with the energy of dissociation of the  $H_2$  molecule, obtained from actual experimental data. Heitler and London have shown that in all cases (*e.g.*,  $O_2$ ,  $N_2$ ...) where molecules are formed of non-polar constituents, the forces are to be ascribed to resonance interactions of pairs of electrons in each atom.

#### *Spectra of Nonpolar (Atom) Compounds.*

The spectra of atom compounds have been studied by a large number of workers, and Franck<sup>3</sup> has given a general theory of their prominent features. The absorption spectra usually consist of bands, sometimes followed by continuous absorptions. For example, the absorption spectra of halogens consist in the visible region, of bands, which all terminate on the short wave-length side in continuous absorption. According to Franck, the molecule in the unexcited state consists of two atoms in the normal state, *e.g.*, in the case of  $I_2$ , both atoms are in the  $^2P_{3/2}$  state.

When light falls on it, one atom changes to the metastable state  $^2P_{1/2}$ , attended with the usual vibration-rotation disturbances; the

continuous absorption corresponds to the splitting of the molecule into atoms with the states  $^2P_{\frac{3}{2}}$  and  $^2P_{\frac{1}{2}}$ . From this theory, Franck deduces the important conclusion that if  $\nu_0$  be the limiting frequency of absorption

$$h\nu_0 = D + h\left(^2P_{\frac{3}{2}} - ^2P_{\frac{1}{2}}\right) \quad \dots \quad \dots \quad \dots \quad (7)$$

where  $D$  is the heat of dissociation of the halogen. From this relation, since  $\nu_0$ ,  $^2P_{\frac{3}{2}}$  -  $^2P_{\frac{1}{2}}$  are all known from spectroscopic data, it is possible to deduce the heat of dissociation  $D$ . The values obtained from such considerations agree remarkably well with the heats of dissociation of halogens as actually determined by Bodenstein and Starck<sup>4</sup> from thermochemical data.

Franck's relation (equation 7) has been extended to the case of other atom-compounds besides  $H_2$ .<sup>5</sup> Wherever the spectroscopic data are well known, the relation has been found to lead to correct results.

#### *Intermediate Compounds.*

There are compounds like the hydrogen halides, and silver halides which were found to satisfy none of the above conditions laid down either for atom-compounds or polar compounds. The three hydrogen halides  $HCl$ ,  $HBr$ ,  $HI$  <sup>6</sup> and (probably also  $HF$ ) show no trace of band-absorption, but perfectly continuous absorption beginning from a long wave-length limit. But the long wave-length limit does not apparently satisfy Franck's relation (equation 7) which was written in the case of  $NaCl$ . On account of this discrepancy, Franck was led to believe that the hydrogen halides were atom-compounds. But this hypothesis is inconsistent with two well established facts, (1) that all the halides are diamagnetic.....this can happen only if the molecule consists of constituents with inert gas shells (e.g., of  $H^+Cl^-$  in  $HCl$ ). If they consist of  $H$  and  $Cl$ , then the  $^2S_{\frac{1}{2}}$ -term of  $H$  cannot be compensated magnetically by the  $^2P_{\frac{3}{2}}$  or  $^2P_{\frac{1}{2}}$  state of  $Cl$ , hence the molecule would be paramagnetic ;

(2) the absence of band absorption throughout the whole quartz and probably fluorite region, which is difficult to understand if the substances are atom-compounds.

On account of these doubts and as a study of the current literature showed that the works on which Franck's conclusions were based were not probably carried out with much care, I directed A. K. Dutta in my laboratory to make a quantitative study of the absorption spectra of these halides at different pressures, and find out their extinction coefficient for light of different frequencies. The wavelength at which this quantity just vanished was taken as Franck's limit  $\nu_0$ . This was found in the case of HBr and HI to be widely different from the values assumed by Franck from eye-estimation, but instead they perfectly agreed with formula for ionic compounds, thus proving that HBr and HI are ionic compounds like the alkali halides. The absorption curves in HBr and HI are found to be very gradual while in the case of alkali halides they are rather steep. Hence eye-estimation in the case of the hydrogen halides leads to great error.\*

*Silver and Thallium Halides.*—The halides of silver and thallium have been found to give band absorption, as well as continuous absorption. The band-absorption of silver halides has been studied with great care by Brice<sup>7</sup> and thallium halides by Butkow,<sup>8</sup> but as yet no satisfactory explanation of their spectra has been found.

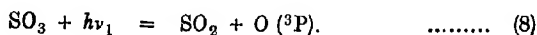
*The Polyatomic Compounds.*—Not much work has yet been done on the polyatomic compounds. Their spectra, in emission as well as in absorption, have for the most time remained unstudied. For this reason, and with a view to collecting information, a number of experiments was carried out in my laboratory and some of them appear to be quite promising. A few are reported below.

#### *Absorption Spectra of Saturated Oxides*

Next to halides, one would naturally try the oxides and sulphides, but these are for the most part very refractory, and attention was therefore confined to saturated oxides like  $\text{SO}_3$ ,<sup>9</sup>  $\text{N}_2\text{O}_5$ ,  $\text{TeO}_3$ ,  $\text{MoO}_3$ , which are either gaseous or can without much difficulty be obtained in the vapour form. It is known that unsaturated oxides like  $\text{SO}_2$ ,  $\text{NO}$ ,  $\text{NO}_2$ ,... give band absorption. As their spectra were well studied they were not taken up. A. K. Dutta<sup>10</sup> (in some works in collaboration with P. K. Sen Gupta) has shown that all these saturated oxides give continuous absorption. The result in the case of  $\text{SO}_3$  is typical and promises to be quite

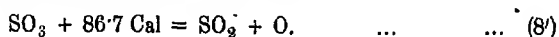
\* The work on HCl could not be completed owing to Mr. Dutta's transference to Benares.

interesting. It partially decomposed into  $\text{SO}_2$  at ordinary temperature, but the proportion of  $\text{SO}_2$  can be reduced by using an excess of oxygen. The absorption spectrum of  $\text{SO}_3$  shows a sharp cut at  $\lambda$  3800 Å followed by a patch of retransmitted light with a second cut at  $\lambda$  2300 Å. Beyond this it was not possible to proceed as a fluorite vacuum spectrograph was not available. Dutta interpreted the results as follows:—the first cut corresponds to the process,

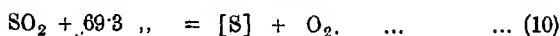
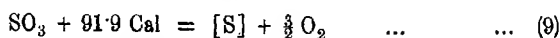


Normal  $\text{SO}_3$  is supposed to consist of  $(\text{SO}_2)^+$  and  $\text{O}^-$ . When light falls on the molecule, the electron absorbs the energy and leaves O in the normal state ( $^3\text{P}$ ), and the result is dissociation into  $\text{SO}_2$  and  $\text{O} (^3\text{P})$ . If this idea be correct, the heat of dissociation of  $\text{O}_2$  can be easily calculated from the value of  $\nu_0$  with the aid of thermochemical data as follows:—

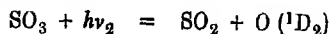
$\lambda$  3300 Å corresponds to 86.7 Cal, hence



From thermochemical determinations, we have



From equations 8' to 10 we get  $\text{Do}_2 = 128 \text{ Cal}$ , which as Dutta shows is in good agreement with other reliable determinations of this quantity from other sources. A further support in favour of the hypothesis is afforded by the interpretation of the second cut. This is interpreted as,



i.e., the pulse  $h\nu_2$  decomposes  $\text{SO}_3$  into  $\text{SO}_2$  and an oxygen atom in the next excited state of the O-atom, viz.,  $^1\text{D}_2$ . If this hypothesis be true,  $h(\nu_2 - \nu_1)$  should be  $\text{O} (^1\text{D}_2) - \text{O} (^3\text{P})$ . The latter value has been found very exactly from spectroscopic data by Frerichs and Paschen, and is equal to 1.90 volts.  $h(\nu_2 - \nu_1)$  in  $\text{SO}_3$  is found to have the value 1.70 volts. The agreement is not quite exact, but this is probably because the beginning of absorption has not yet been fixed with the accuracy needed for the purpose. There are other theoretical arguments to account for the discrepancy, but these are not reproduced here as the treatment will be too long.

*Possibility of getting Auroral Radiation from Post-dissociation  
Radiation of Irradiated SO<sub>3</sub>.*

From the above interesting work on the spectrum of SO<sub>3</sub> and other saturated oxides, which are quite similar, Dutta has drawn a conclusion of the highest importance. If SO<sub>3</sub>, on being irradiated with light frequency  $\nu_2$ , breaks up into SO<sub>2</sub> and an oxygen atom in the  $^1D_2$ -state, what will happen to the excited oxygen atom? It will either dissipate its energy by collisions of the second type with other atoms and molecules present, or if collisions be prevented by lowering the pressure, the only thing it can do is to revert back to the normal state after radiation of the line  $\lambda = ({}^3P_{0,1,2} - {}^1D_2)$ . These lines have the wavelengths  $\lambda$  6300, 6363 Å and have been obtained in the laboratory by Paschen and Frerichs<sup>11</sup> from pure discharge through a vacuum tube containing pure oxygen. They have been called "Red Auroral Lines" on account of their connection with the celebrated Green Auroral line  $\lambda$  5577 Å which has been now definitely assigned to the transition  ${}^1S_0 \rightarrow {}^1D_2$  of the oxygen atom. It may be mentioned here that the normal oxygen atom which has got electronic constitution  $2p^4$  can, according to Pauli's Principle, take up five equilibrium states denoted by  ${}^3P_{0,1,2}$ ,  ${}^1D_2$ ,  ${}^1S_0$ . In the triplet terms, the spins of three out of four electrons have the same direction, while the spin of the fourth has the reverse direction. In  ${}^1D_2$  and  ${}^1S_0$  two electrons have their spins in one direction, two others in the opposite direction. To go from  ${}^1D_2$  or  ${}^1S_0$  to  ${}^3P$ -states, only one electron has to reverse its spin. Usually the transitions between these states are forbidden, but they do take place when the atom excited in the metastable state is under a strong electric or magnetic field, or is in such attenuated condition that collisions are rare, and the atom has nothing else to do than to revert back to its normal state by running its usual life.

The interest of these different states of the O atom lies in the fact that they have afforded an explanation of the green line  $\lambda$  5577 Å which was observed in the spectra of aurora, and was at one time ascribed to a hypothetical element "Geocoronium".<sup>12</sup> It has since been observed in the spectrum of the night-sky, and seems to be a general characteristic of the upper atmosphere. The origin of this line was a matter of controversy for a long time, till from a series of works, it was established beyond doubt that it is due to the  ${}^1S_0 \rightarrow {}^1D_2$  transition of O. But the way in which it originates in the upper atmosphere

has not yet been made clear. It is extremely probable that the  $^3P_{0,1,2} - ^1D_2$  lines, at least the first two of them should come in the auroral spectrum as well as in the spectrum of the night-sky, but this result, announced by Sommer<sup>12</sup> has been challenged by Grotrian.<sup>13</sup> Probably the intensities of the so-called red auroral lines are rather small compared with that of the green auroral line.

If Dutta's theory of the absorption spectrum of  $SO_3$  and other higher oxides be true, then  $SO_3$  illuminated with  $\lambda < 2300\text{\AA}$  should give us the real auroral lines; and when illuminated with  $\lambda < 1700\text{\AA}$  should give us the green auroral lines. These experiments have been tried by Dutta, and the appearance of one of the lines, viz.,  $\lambda 3300\text{\AA}$  seems to be fairly well-established. The experiments which are rather difficult to carry out, are being continued with greater effort.

#### *Spectra of Polyhalides.*

No work seems to have been carried out so far on the spectra of the halides of Mg, Al and Si. A preliminary investigation in the Allahabad Physical Laboratory by S. C. Deb<sup>14</sup> has shown that all these halides give a continuous absorption spectrum beginning from a long wave-length limit. A. K. Dutta<sup>15</sup> investigated the absorption of  $CCl_4$ ,  $SiCl_4$  and  $SnCl_4$  and found that they are exactly similar to the spectra of  $NaCl$ . From these experiments it appears that the frequency limit  $\nu_0$  is given approximately by the relation,

$$h\nu_0 = R/n \quad \dots \quad \dots \quad \dots \quad (11)$$

where  $R$  is the atomic heat of formation and  $n$  is the valency.

The quantity  $R$  cannot be directly determined but has to be deduced out of thermochemical data from the general formula

$$R = Q + L_M + \frac{n}{2} D_{Ha_2} - L_{M_{Ha_2}}$$

where  $Q$  is the heat of formation,  $D_{Ha_2}$  = heat of dissociation of the halogen; and  $L$  = latent heat of vaporization.

Now  $L_M$  and  $L_{M_{Ha_2}}$  the latent heats of vaporization of the element forming the cation, and of the halide are not known with certainty in most cases. For  $C$  it varies from 140 Cal to 280 Cal, unless these quantities are accurately determined, it is not possible to say whether the relation (11) is exact or not.

In the course of these investigations it has appeared that in the case of those compounds where the molecule does not possess a spherical symmetry, the above generalisation fails to be true. The correctness of this statement is rendered probable from the fact, that in the case of spherical symmetry it can be supposed that the valency bond is distributed equally amongst the  $n$ -halogen ions, so that only  $1/n$ th part of the total binding energy is required to break one of the halogen atoms from the molecule.

But where this spherical symmetry is wanting, we can suppose the Franck-Condon curves for these molecules to be shifted to the right according to the degree of asymmetry; the result is that the beginning of absorption shifts to the ultraviolet side. This is perhaps the case in the example of aluminium halide molecules. For aluminium halide, the thermochemical data are more or less accurately known. We find in this case that the value of  $R/n$  is in every case less than the value derived from  $L_M$ . Such is the case with the mercury halides as well, which is also studied by Deb and Mohanty in this Laboratory; in these cases thermochemical data are all available.

We thus find that the generalised Franck's relation,  $h\nu$  corresponding to  $R/n$  holds, only strictly for alkali halides and halides possessing a spherical symmetry in their structure. As we take  $MgCl_2$ ,  $AlCl_3$ ,  $SiCl_4$  there is probably progressive departure from the relation (11).

#### *Saturated Halides showing Bands in Absorption.*

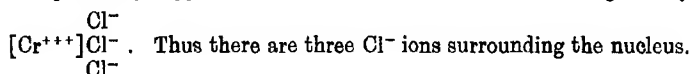
Apparently band absorption in such cases is impossible from the considerations given above. But the absorption spectra of silver and thallium halides which are chemically similar to alkali halides show, as has been said previously, band absorption in addition to continuous absorption. It has been established in the case of silver halides in this laboratory that the continuous absorption phenomena can be interpreted as similar to those of saturated spherically unsymmetrical compounds. But the interpretation of the band absorption still remains obscure. Though no definite solution is yet available, it is clear that molecules whose metallic constituent possesses one or more metastable levels, always give rise to band absorption. To test this point I directed my scholars S. C. Deb and B. Mukherjee to investigate the nature of absorption shown by alkaline earth halides. It is definitely known that the metal constituent of these molecules



have got a stable  $S^2$  orbit and a metastable  $d^{10}$  orbit. So if the above generalisation be correct these compounds ought to show band absorption along with the continuous absorption which is common to every saturated molecule. Deb and Mukherjee<sup>16</sup> investigated several halides of these alkaline earth metals in the Heraeus furnace of my laboratory. In every case there was a band absorption accompanied by continuous absorption similar to the well known case of silver halides.

*Halides of the Transitional Group of Elements and Origin of Colours of the Inorganic Salts.*

Another entirely different class of compounds, chiefly poly-atomic are the halides of the elements of the transitional group. A study of the magnetic moment of these halides in solution shows that the compounds consist of an ionic metallic core surrounded by saturated inert gas type shells. If we take a compound like  $\text{CrCl}_3$  we may suppose the picture of the combination as given by



The magnetic action of these molecules is explained as due entirely to the  $\text{Cr}^{+++}$  core, the  $\text{Cl}^-$  ions contributing nothing to the moment. It is well known that to change a stable configuration such as that of an inert gas type, quite a large amount of energy is required; so the colour, i.e. the absorption of light due to these compounds in the visible region, cannot be due to any change primarily occurring in the  $\text{Cl}^-$  ions. The probability remains that the colour arises from the reaction of light on  $\text{Cr}^{+++}$  ions. This contains in the free state an incomplete  $d^3$ -shell, giving rise to certain number of quartet  $^4X$  and doublet  $^2Y$  terms. 'L' Coupling in compounds ceases to be of importance in a molecular formation, which subdivides themselves along the figure axes, while S- vectors take up either parallel or antiparallel directions. We can therefore suppose that the action of light consists in changing the spin of one of the component electrons in the  $d^3$ -shell. The energy required in this process is in every case small, and actually falls within the range indicated in the visible spectrum. This is the result with almost all ions of the elements of the transitional group.

A number of experiments may be designed to test this hypothesis. Owing to the limited capacity of this laboratory the absorption spectra

of a few chlorides of the transitional group were tried. Due to various reasons chiefly among them the unstability of the compounds in vapour state at a high temperature, not many of these compounds could be satisfactorily investigated, but those investigated ( $\text{CrCl}_3$ ,  $\text{FeCl}_3$ ) showed without any ambiguity the presence of band absorption at the very position predicted by the hypothesis of the change of spin vector due to the action of light. S. C. Deb<sup>17</sup> working under my suggestion showed that in the case of  $\text{CrCl}_3$ , absorption bands were obtained in the blue violet region extending slightly into the ultra-violet, which is certainly due to reaction of light on the  $d^3$  shell of  $\text{Cr}^{+++}$  ion, the spin moments of the electrons in the normal state for which level being parallel, give rise to a  $4x$  term. The action of light would be to turn the spin of one of the electrons in the opposite direction giving rise to band absorption; continuous absorption has also been observed, probably corresponding to the splitting of  $\text{CrCl}_3$  into  $\text{CrCl}_2$  and  $\text{Cl}$  but owing to absence of thermochemical data, viz., heat of vaporisation of  $\text{CrCl}_3$  and  $\text{Cr}$  the continuous absorption spectra could not be interpreted.

*Thermochemical Data from Absorption Experiment.*

In cases where the theory is on safe grounds, the process can be reversed, and thermochemical data can be obtained from results of absorption experiments. As an illustration of this method, reference can be made to certain works which have been performed in this laboratory. M. S. Desai<sup>18</sup> has been able to determine the heat of dissociation of Fluorine by studying the absorption spectra of alkali fluorides and utilising relation (4). The value which he obtains, 78 Cal, is the first estimate of this important quantity. It has still to be confirmed by independent determinations. He also studied the absorption spectra of lithium halides, and determined the heat of evaporation of lithium<sup>19</sup> from equation (4). This was found to be 29.3 Cal. After his result was published, there came a paper by A. Bogros in the *Annales de Physique* (March, 1932, p. 200) where measurements of vapour pressure of  $\text{Li}$  are reported. The value of latent heat derived from these measurements is 28.2 Cal which is in very good agreement with Desai's value. Similarly, A. K. Dutta<sup>20</sup> determined the absorption spectra of  $\text{N}_2\text{O}$  and found it to be perfectly continuous beginning from  $\lambda 2750\text{\AA}$ . From this, and using other thermochemical data he obtained a value of 204 Cal for

the heat of dissociation of  $N_2$ . This is probably the best value of this quantity so far determined.

*Conclusion.*

From the above short and imperfect sketch, the chemical reader will probably find that spectroscopy is making itself increasingly useful to the chemist. Space does not permit me to discuss the important contributions by Herzberg and on the theoretical side, of the works in recent years by Slater, Heitler, London, Born and Weyl<sup>21</sup> who are applying wave mechanical methods for finding out energy values of chemical bonds and explaining other features of chemical combination. These investigations are sure to throw much light on these time-honoured problems.

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## Die Neueste Entwicklung der Polysaccharid-Chemie.

VON

HANS PRINGSHEIM.

Seit vor einem Jahre die 3. Auflage der Polysaccharide zum Abschluss gebracht wurde,\* sind wieder eine grosse Zahl von Veröffentlichungen auf diesem vielbearbeiteten Wissenschaftszweige erschienen, deren Hauptergebnisse wir an der Hand der wichtigsten zusammenfassen wollen.

### A. Polysaccharide erster Ordnung oder Oligosaccharide.

Auf synthetischem Gebiete wurde ein neues nichtreduzierendes Disaccharid aus zwei Glukose-Resten durch die Vereinigung der Brigl'schen Triacetyl- 1: 2- Anhydroglukose mit Tetra-acetylglukose gewonnen (Haworth u. Hickinbottom, *J. Chem. Soc.*, 1931, 2847) und *neo-Trehalose* genannt. Merkwürdigerweise zeigt dieses Disaccharid keine Uebereinstimmung in der optischen Drehung mit einer der drei sterischen Isomeren, welche sich nach der Hudson'schen Regel für die  $\alpha\alpha$ ,  $\alpha\beta$  und  $\beta\beta$ -Form des Glukosido-glukosids aus zwei Gluko-pyranose-Resten errechnen lässt. Dieser Punkt bedarf also noch der Aufklärung.

Eine Synthese der Cellobiose, wenn auch in geringer Ausbeute ist Helferich gelungen, (Helferich u. Bredereck, *Ber.*, 1931, 64, 2411) ausgehend von der Beobachtung, dass sich das 2: 3: 4-Triacetyl- $\beta$ -Methylglukosid durch acyl-wandering in 2: 3: 6- $\beta$ -Methylglucosid umwandeln lässt, welches mit Acetobromglukose zu Hept-Acetyl- $\beta$ -Methylcellobiosid kondensiert wurde, von dem aus die *Cellobiose* selbst zugänglich ist.

Besonders interessant ist die Gewinnung eines neuen Stickstoffhaltigen Disaccharides, der *Chitobiose* aus Chitin. Es wurde aus diesem Polysaccharid auf zwei verschiedene Weisen erhalten, durch acetolytische Spaltung (Bergmann, Zervas u. Silberkweit, *Ber.*, 1931, 64, 2436) wie auch durch Hydrolyse von Chitin mit überkonzentrierter Salzsäure (Zechmeister u. Toth, *Ber.*, 1931, 64, 2028).

H. Pringsheim, *Die Polysaccharide*, Berlin, Julius Springer 1931, dort die Literatur für die früheren, herangezogenen Arbeiten.



Schwanken. Hier entwickelt sich nach und nach eine Auffassung von der relativen Spezifität, welche, wenn sie bis in ihre letzten Konsequenzen verfolgt würde, das Spezifitätsproblem zu einer völligen Verwirrung, ja, zu einer Aufhebung dieser für die Entwicklung der Biologie der Fermente so wichtigen Grundlage führen würde. Zwar scheint der Unterschied zwischen den  $\alpha$ - und  $\beta$ -Glykosidasen, der Emil Fischer zuerst zu der Prägung des anschaulichen Bildes vom Schloss und Schlüssel geführt hat, nach einigem Schwanken nicht angetastet zu werden, (Helferich u. Appel, *Z. physiol. Chem.*, 1932, 205, 231; vgl. *Nachschrift.*, 247) aber die Frage nach der Identität der Glykosidasen mit den Disaccharasen und den Polyasen, die von Weidenhagen (*Erg. der Enzymforschung*, Leipzig, 1932) zur Grundlage einer vereinfachten Spezifitätstheorie gemacht worden ist, wird so mit der Affinitätsfrage verknüpft, dass man sich nicht mehr herausfinden kann. Dass die  $\alpha$ -Glukosidase der Hefe mit der Saccharase identisch sei, kann als definitiv widerlegt angesehen werden. (Karström, *Biochem. Z.*, 1931, 231, 399; Myrbäck, *Z. physiol. Chem.*, 1931, 198, 196). Aber auch die prinzipielle Identität der  $\alpha$ -Glukosidase mit der Maltase selbst ist nicht aufrecht zu erhalten, nachdem im Gerstenmalz, im *Aspergillus oryzae* und *Wentii* ein die Maltase spaltendes Ferment aufgefunden worden ist, das dieses Disaccharid ebenso stark wie die Hefe-Maltase anzugreifen vermag, ohne auf  $\alpha$ -Methylglukosid von irgendwelcher Wirkung zu sein. (Pringsheim, Borchardt u. Loew, *Z. physiol. Chem.*, 1931, 202, 23; Pringsheim u. Loew, ebenda im Druck; Myrbäck, ebenda, 1932, 205, 248.) Dem negativen Spaltungsversuch gegenüber wird immer der Einwand offenbleiben, die mangelnde Affinität der Gluko-Maltase in den genannten Ferment-Präparaten als Erklärung für die nicht gelungene Spaltung des  $\alpha$ -Methylglukosides heranzuziehen, trotzdem hier schon ein Affinitätsunterschied von 1:100 obwalten müsste. Es besteht immer noch die Möglichkeit zu sagen, dass ebenso wie die Identität der Hefe-Saccharase mit der Hefe-Raffinase trotz ihrer durch einen ausgesprochenen Affinitätsunterschied gegenüber den beiden Substraten begründeten Abweichung in der Kinetik der Ferment-Hydrolyse erklärt und gleiche Geschwindigkeit der enzymatischen Spaltung nur bei Substratkonzentrationen gefunden wurde, die den verschiedenen Affinitäten entsprechen, auch in unserem Fall dieses Erklärungsprinzip herangezogen werden kann. Geht man aber in dieser schlussfolgerung weiter und behauptet man die Identität der  $\beta$ -h



Fruktosidase der Hefe mit der Inulinase (Weidenhagen, *Naturwiss.*, 1932, 20, 254), trotzdem das Verhältnis der Hydrolyse hier nur wie 1:7500 ist, dann kommt man in Gefahr, den Affinitätsbegriff zu überspannen. Abgesehen davon, dass der Beweis für die Abwesenheit einer geringen Menge einer Inulinase in einem so stark konzentrierten Hefe-Fermentpräparat nicht erbracht ist, setzt man sich der Gefahr aus, dass in jedem Falle, in welchem die Nichtspaltung eines spezifischen Fermentsubstrates behauptet wurde, die Anreicherung des eingebrachten Fermentpräparates in einem ungemessenen auf experimentellem Wege kaum noch darzustellenden Massstabe verlangt wird. Und ganz ähnlich liegen die Verhältnisse bei dem Vergleiche verschiedener Glykoside als Fermentsubstrate untereinander, z. B. von Glukosiden, Galaktosiden, Xylosiden usw. mit verschiedenem A-Glykon (Helferich u. Appel, *loc. cit.*). Besonders verwirrend ist, dass der Begriff der Spezifität mit der Frage der natürlichen Anpassung der Fermente nicht verbunden werden kann, weil ja als spaltbare Substrate naturfremde Stoffe, wie z. B. das Methylglukosid-6-Bromhydrin oder Phenolglukoside, herangezogen werden können.

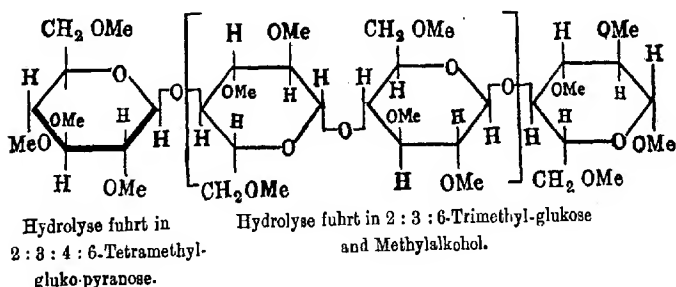
#### B. Polysaccharide zweiter Ordnung oder komplexe Polysaccharide.

##### *Cellulose.*

Dass die Cellulose eine fortlaufende Kette von Glukose-Resten bildet, die nach dem Prinzip der Cellobiose-Bindung verknüpft sind, wird immer schärfer begründet und kann wohl als endgültig angesehen werden. Die direkte Isolierung kristallisierter Oligosaccharide aus dem Abbauprodukte der Cellulose durch überkonzentrierte Salzsäure ist in letzter Zeit sehr vervollkommenet worden, (Zechmeister u. Toth, *Ber.* 1931, 64, 864.) wobei neben der Cellobiose die *Cellotriose* und die *Cellotetraose* in schön kristallisierter Form erhalten worden sind; auch eine *Hexsaose* ist kristallisiert beschrieben worden; für sie wird aber die Einheitlichkeit noch nicht in Anspruch genommen. Der Beweis für der fortlaufende Cellobiose-Bindung ist besonders gelungen durch die Isolierung kristallisierter und in Gestalt ihrer Glukoside destillabler methylierter Oligosaccharide mit bis zu 4 Glukose-Resten (Haworth, Hirst u. Thomas, *J. Chem. Soc.*, 1931, 824; Freudenberg, Friedrich u. Bumann, *Annalen*, 1932, 494, 41). Die methylierte Cellotriose wurde inzwischen (Freudenberg u. Nagai, *Annalen*, 1932, 494, 63) auf einem schönen Wege synthetisiert und mit dem beim Abbau aus Cellulose gewonnenen identisch befunden. Dadurch

ist nun mit Sicherheit bewiesen, dass mehr als zwei glukosidische Bausteine in der Cellulose nach dem  $\beta$ -1:4-Prinzip untereinander verknüpft sind. Aber darüber hinausgehend werden von Freudenberg an den genannten Abbauprodukten auf grund der Gesetze der optischen Superposition Errechnungen angestellt, die dieses Bauprinzip auch für die ganze Kette sehr wahrscheinlich machen.

Diskutabel ist noch die Länge der Ketten und die Frage der möglichen Endgruppen. Sie scheint durch neue Ergebnisse beantwortet zu werden, (Haworth, *Ber.*, 1932, 65, 60) aus denen hervorgeht, dass ich bei der Hydrolyse einer Menge von 200 g. reiner Trimethyl-Cellulose, 2:3:4:6-Tetramethyl-Gluko-Pyranose, entsprechend



obenstehender Formulierung in einem Massstabe isolieren liess, demzufolge die Cellulose nicht weniger als 50 und nicht viel mehr als 100 Cellobiose-Reste enthalten kann. Das entspricht einem Molekulargewicht von 20000 bis 40000 stellt aber nur eine untere Grenze dar.

Ein neuer und interessanter, möglicherweise praktisch verwertbarer Abbau der Cellulose wurde von Schlubach beschrieben (Schlubach, Elsner u. Prochowinck, *Z. angew. Chem.*, 1932, 45, 245). Er fand, dass 100% ige Salzsäure, d. h. trockenes Chlorwasserstoffgas instand ist, Cellulose glatt und vollständig zu niedermolekularen Glukose-Anhydriden abzubauen, die spielend in Wasser löslich sind. Druck, Temperatur und Zeit spielen hierbei eine ausschlaggebende Rolle. So waren trockene Baumwoll Linters durch trockenen Chlorwasserstoff unter 43 3/4 at. Druck bei 20° innerhalb 10 Stunden vollständig in wasserlösliche Produkte umgewandelt. Das Abbauprodukt stellt ein weisses Pulver dar, das hauptsächlich aus 1-, 2- und 3-molekularen Anhydriden der Glukose besteht, welche durch 1% ige Salzsäure so gut wie vollkommen in Glukose umgewandelt werden können. Dabei wurde die interessante Beobachtung gemacht, dass Chlorwasserstoff unter Druck auch reduzierende einfache Zucker anhydriert und

zugleich diese Anhydride polymerisiert, also eine Reversion bedingt, die auch beim Abbau im allgemeinen von Bedeutung sein wird. Die Schlubach'sche Reaktion, die auch andere hochmolekulare Stoffe, wie Stärke, ja Seidenfibroin, Wolle, Horn und ähnliche Naturstoffe zu niedermolekularen Anhydriden abzubauen gestattet, verläuft, ohne irgend eine Hydrolyse, so dass also Umlagerungen, im speziellen Falle bei der Cellulose Sauerstoffbrückenverschiebungen, für den Abbau verantwortlich gemacht werden müssen. In ähnlicher Weise dürfte der Abbau der Cellulose zu erklären sein, den sie zu niedermolekularen nicht reduzierenden Spaltstücken erleidet, wenn man ihr Acetat in chloroformiger Lösung bei Gegenwart geringer Mengen Benzolsulfosäure kocht (Pringsheim u. Ward, *Cellulosechemie*, 1932, 13, 65).

#### *Stärke und Glykogen.*

Sehr viel weniger Einigkeit als bei der Cellulose herrscht über den Aufbau der beiden genannten Reserve-Polysaccharide. Während Haworth auf dem Standpunkt steht, dass die Hüll- und Inhaltssubstanz der Stärke sich nur in ihren physikalischen Eigenschaften unterscheiden, dass Amylose, Amylopektin und Glykogen das gleiche Aufbauprinzip besitzen müssen, neigen Samec und Waldschmidt-Leitz (*Z. physiol. Chem.*, 1931, 203, 16), der früher von mir diskutierten Meinung zu, dass die Amylo- und Erythro-Körper der Stärke von einander verschiedene Atomgruppierungen aufweisen. Die chemischen und fermentochemischen Resultate stehen also hier in einem gewissen Gegensatz und erst die Zukunft wird entscheiden können, ob die Gefahren der Umlagerung bei diesen labilen Polyosen, die ich nach meinen Erfahrungen an den kristallisierten Abbauprodukten der Stärke, den Polyamylosen, für ausserordentlich gross halte, auf dem chemischen oder auf dem enzymatischen Abbauewege grösser sind. Jedenfalls sind die von mir in meinen Polysacchariden diskutierten Einwände gegen die Auffassung der Konstitution der Stärke als einer fortlaufenden Maltose-Kette bisher nicht widerlegt worden (Haworth u. Percival, *J. Chem. Soc.*, 1931, 1842) stützt sich bei seinen Versuchen wieder auf die Spaltungsprodukte der methylierten Stärke, die durch Acetbromid in Hexamethylmaltobiose ungewandelt wird, deren Konstitution er einwandfrei festlegt. Demgegenüber ist jedoch hervorzuheben, dass sich auf diesem Wege ja gewiss nur die Maltose-Bindung zwischen paaren Glukose-Resten beweisen liesse, während sie den fortlaufenden

Wechsel zwischen pyroiden und furoiden Glukose-Baustücken in der Stärke noch nicht ausschliesst. Aber selbst das Vorhandensein der Maltose-Bindungen im Stärkemolekül überhaupt erscheint noch nicht endgültig bewiesen, da für die Gewinnung der methylierten Stärke von Stärkeacetat ausgegangen wird, bei dessen Bereitung Umlagerungen möglich sind. Solche sind auch bei der Spaltung der Methylostärke durch Bromacetolyse nicht ausgeschlossen. Der gleiche Standpunkt der fortlaufenden Maltose-Bindungen wird auch in der neuesten Arbeit von Freudenberg (Freudenberg, Friedrich u. Bumann, *loc. cit.*) vertreten, wobei in ähnlicher Weise wie bei der Cellulose von methylierten Acetolierungs-Abbauprodukten der Stärke ausgegangen wird, welche durch Destillation voneinander getrennt werden. Abgesehen davon, dass hier die Umlagerungsmöglichkeiten bei der direkten Acetolyse der Stärke bei einer Temperatursteigerung bis zu 88° ausserordentlich gross erscheinen, muss darauf hingewiesen werden, dass die Destillationsprodukte in diesem Falle im Gegensatz zur Cellulose nicht kristallin sind, und dass ihre Zugehörigkeit zur Maltose-Reihe aus dem Drehwerte auf einem von Umwegen nicht freien Verfahren errechnet wird und sich nicht wie bei der Cellulose auf den Vergleich mit einem synthetischen Methylo-Trisaccharid stützt. Nach dem bei der Cellulose eingehend beschriebenen Verfahren soll nun auch das Problem der Endgruppen im Amylose-Anteil der Stärke gelöst worden sein (Haworth, *Nature*, 1932, 129, 365). Auf Grund der daraufhin angestellten Berechnungen soll die durchschnittliche Kettenlänge der Stärkeamylose mindestens 20 Glukose-Reste betragen. Demgegenüber erwähnt jedoch Freudenberg in einer Anmerkung auf Seite 54 seiner Annalenarbeit, dass bei den mit der Stärke ausgeführten Operationen die Gefahr der Hydrolyse noch grösser sei als bei der Darstellung der Acetyl-Cellulose, von der ausgehend Haworth seine Methylo-Cellulose erhält, und er hebt ganz mit recht hervor, dass die Zahl der freien Aldehydgruppen in der Stärke geringer ist, als so kurze Ketten erwarten lassen würden. Stärke reduziert nämlich die Fehling'sche Lösung gar nicht. Die Annahme bleibt also immer noch offen, dass solche Reserve-Polysaccharide wie Stärke und Glykogen keine offenen sondern an den Enden zu Ringen verschmolzene Ketten darstellen, die gewisse Abbaureaktionen am besten zu erklären gestatten (vgl. Die Polysaccharide, Kapitel 10). Solche Formengebilde werden wir beim Inulin noch antreffen. Ein Beweis für den von Freudenberg (*J. Soc. Chem. Ind.*, 1931, 50, 287) diskutierten anhydri-

sehen Abschluss der Stärkekettten oder ihrer Bruchstücke, z. B. der Polyamylosen, liegt bisher nicht vor.

Fortschritte sind auf dem Gebiete des fermentativen Abbaus der Stärke zu verzeichnen. Dass es zwei Typen von Amylasen, die  $\alpha$ -oder Dextrinogenamylase und die  $\beta$ -oder Saccharogenamylase gibt, erscheint nun definitiv als bewiesen. Hierzu haben die neueren Untersuchungen von Ohlsson (*Z. physiol. Chem.*, 1930, **189**, 17) viel beigetragen. Wir wissen jetzt, dass die Pankreas- und die Speichel-Amylase der Hauptsache nach zu den  $\alpha$ -Amylasen gehören, während in der Malz-Amylase mehr  $\beta$ -als  $\alpha$ -Amylase vorhanden ist. Die Kartoffel-Amylase nimmt eine Zwischenstellung ein (Borchardt u. Pringsheim, *Biochem. Z.*, 1931, **139**, 193). Die Gersten-Amylase wurde kürzlich als  $\beta$ -Amylase charakterisiert (Nordh u. Ohlsson, *Z. physiol. Chem.*, 1932, **204**, 89). Waldschmid-Leitz (*Naturwiss.*, 1932, **20**, 234) hat jedoch die sehr interessante Feststellung gemacht, dass neben der  $\beta$ -Amylase in der ungekeimten Gerste eine inaktive Vorstufe der  $\alpha$ -Amylase vorhanden ist, welche erst durch einen Aktivator in die wirksame Dextrinogenamylase übergeht. Dieser Aktivator entsteht erst bei der Keimung, er befindet sich also im Gerstenmalz und konnte hieraus isoliert werden (Waldschmid-Leitz u. Purr, *Z. physiol. Chem.*, 1931, **203**, 117). Die Abtrennung der hier wirksamen "Amylokinase" geschah auf Grund der kolloidchemischen Erfahrungen für die Trennung der Fermente von einander und von ihren Aktivatoren, die Waldschmid-Leitz mit so grossem Erfolge schon auf Eiweiss-spaltende Fermente angewandt hat. Der neu entdeckte Aktivator der Amyolyse, die "Amylokinase" muss von dem zuerst beschriebenen dem "Komplement der Amylasen" verschieden sein, da dieses nicht dazu imstande ist, die inaktive Form der Gersten  $\alpha$ -Amylase in die aktive umzuwandeln. Dagegen wurde gezeigt, (Pringsheim, Borchardt u. Hupfer, *Biochem. Z.*, 1931, **238**, 476) dass sich die aktivierende Wirkung des Hefe-Komplementes auch durch das kristallisierte Tripeptid, Glutathion, erreichen lässt. Im Gegensatz zu anderen enzym-aktivierenden Wirkungen tritt hier die oxydierte Form des Glutathion in Tätigkeit (Pringsheim, Borchardt u. Hupfer, *Naturwiss.*, 1932, **20**, 65). Es muss aber eine spezifische Beziehung zu der im Glutathion enthaltenen schwefelhaltigen Aminosäure vorhanden sein, da wir auch oxydiertes cystein nicht aber die Dithio-Glykolsäure ebenfalls eine S-S Verbindung, wirksam fanden (Pringsheim, Borchardt u. Hupfer, *Biochem. Z.*, im Druck). Am geeignetsten zum Nachweis der Komplement-Wirkung hat sich die

Eiweiss-freie Amylase erwiesen, ((Waldschmid-Leitz u. Reichel, *Z. physiol Chem.*, 1932 **204**, 197), bei der die Ausschläge am grössten sind und bis zu 16% Maltosezuwachs betragen. Durch das Komplement kann man also die Hemmung des Grenzabbaus überwinden und Stärke ganz in Maltose verzuckern. Die Aktivatoren spielen also beim fermentativen Abbau der Stärke ebenso wie beim Eiweissabbau eine bedeutungsvolle Rolle. Ihr Zusammenwirken mit den voneinander abgetrennten einheitlichen Amylasen wird zu weiteren Fortschritten auf diesem so viel und wechselvoll bearbeiteten Gebiete und zu definitiven Abbauprodukten führen.

### *Inulin*

Die Fruktofuranose-Bruchstücke des Inulins entsprechen nach den am Methylo-Inulin gewonnenen Ergebnissen denen des Rohrzuckers. Wie in den "Polysacchariden" erörtert und durch Formeln belegt, hat Haworth das Inulin als ein substituiertes Ethylenoxyd aufgefasst, und er steht auf dem Standpunkt, dass dieses Reserve-Polysaccharid ein gleichmässiggebautes und geschlossenes Ring system aus in 1- und 2-Stellung verketteten Fruktofuranosen darstellt. Um deutlich zu machen, dass dieses Gebilde (vgl. Fig. 1) Neigung zeigen kann, durch Sauerstoffbrücken-Verschiebung Anhydro-Difruktose-Moleküle (vgl. Fig. 2) zu bilden gibt er dem Ringe eine dieser Vorstellung angepasste Zickzack-Formulierung. Auf dieser Grundlage erklärt er die von Jackson (Jackson u. Macdonald, *Bureau of Standards J. Res.*, 1931, **6**, 709), aus dem Hydrolyse-Produkt des Inulins isolierten 3 Difruktose-anhydride als die drei möglichen stereoisomeren Formen der Verkettung dreier in 1:2-Stellung miteinander verbundener furoider Fruktose-Reste, während im Gegensatze dazu Jackson (Jackson u. Macdonald, *ebenda*, 1930, **5**, 1151), seine schön kristallisierten Disaccharidanhydride als Bausteine des natürlichen Inulin-Moleküls ansieht. Die Frage ist noch nicht ganz geklärt, wird jedoch aller Wahrscheinlichkeit nach zugunsten des einheitlichen Bauprinzips des Inulins ausfallen. Früher hat Schlubach den Standpunkt vertreten, dass im Inulin ein kleiner Anteil Glukose, bis zu 5 per cent., vorhanden sei. In seiner neuesten Mitteilung (Schlubach u. Elsner, *Ber.*, 1932, **65**, 519) gibt er jedoch der Ueberzeugung Ausdruck, dass das Inulin nur aus h-Fruktose-Komplexen aufgebaut sei. Offenbar muss also die doch sicher nachgewiesene Glukose einem beigemengten

FIG. 1.

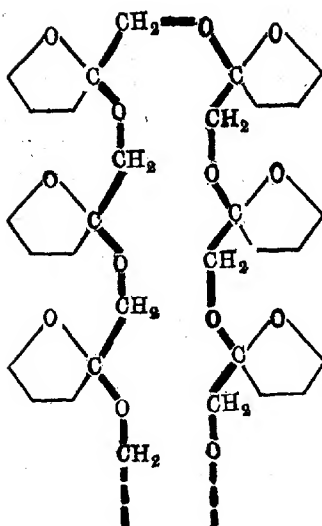
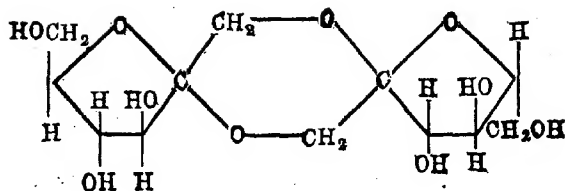


FIG. 2.



Anhydro-difruktose.

Polysaccharid zugehören, das sich hat abtrennen lassen. Durch eine derartige Mischung liesse sich die vergleichsweise grosse Schwankung im Drehwerte verschiedener natürlicher Inuline zwischen 30 und 40° erklären. Wir selbst (Pringsheim u. Ohlmeyer, unveröffentlichte Versuche) haben die Pilz-Inulinase einer sehr wirksamen Reinigungsprozedur durch Adsorption von Aluminiumhydroxyd unterzogen und mit diesem starken Fermente, mit dem man in einem Ansatz 40 g. Inulin spalten kann, nachgewiesen, dass die Fermenthydrolyse bis zu 95 per cent geht und im Hydrolysat eine sehr kleine aber noch fassbare Menge Glukose von ca 1.5 per cent des speziellen Kahlbaum-Inulins vorhanden war.

*Allgemeine Konstitution.*

Aus dem Gesagten geht hervor, dass die komplexen Polysaccharide heutzutage von allen Seiten als Kettenmoleküle aufgefasst werden und dass nun nur bezüglich der Fragen, in sich geschlossene oder offene Ketten, Länge der Ketten und Art des Abschlusses der Ketten, gewisse Meinungsverschiedenheiten bestehen. Die Bedeutung der möglichen Dispergierbarkeit derartiger hochmolekularer Gebilde im Lösungszustande tritt demgemäss hinter der Auffassung von der Kettenstruktur zurück. Sie wird naturgemäss von denjenigen Forschern, welche den hochmolekularen Zustand dieser Naturstoffe erwiesen haben, ziemlich energisch bekämpft. Und doch lässt sich nicht leugnen, dass immer noch gewisse Anhaltspunkte für die aufteilbarkeit der Polysaccharide oder ihrer Derivate in manchen Lösungsmitteln zu kleinen Einheiten vorhanden sind. Bekannt ist ja die Kontroverse über die kryoskopischen Bestimmungen der Acetylcellulose in Eisessig. Dem von Freudenberg erhobenen Einwände gegen die Anwendbarkeit der Kryoskopie in diesen und ähnlichen Fällen tritt eine neue und sehr sorgfältige Untersuchung von Hess entgegen (Garthe u. Hess, *Ber.*, 1931, **64**, 892), die alle Fehlerquellen auszuschalten scheint und auf die bisher nicht erwidert worden ist. Unberechtigt erscheint die Ausstände die Berner (*Ber.*, 1931, **64**, 842, 1531) an unseren kryoskopischen Molekulargewichtsbestimmungen von Inulin und Glykogen, in Acetamid und Formamid, geübt hat. Wir konnten inzwischen zeigen, dass die übertriebene Art der Trocknung bei sehr hoher Temperatur von 110° und langer Dauer für die Ergebnisse Berners verantwortlich ist.

Entscheidende Bedeutung für die Frage der Dispergierbarkeit kommt den Polyamylosen zu, die zum Beispiel in Gestalt ihrer Acetate in manchen Lösungsmitteln, entsprechend ihrer Molekulargrösse in den anderen verteilt, zu ihrer kleinsten möglichen Einheit reagieren. Zu diesem Fragenkomplexe gehört auch die Unterscheidung der Diamylose von der Tetraamylose. Unsere Beobachtung, dass die Diamylose durch den Gehalt einer gewissen Menge Alkohol (oder vielleicht eines anderen Lösungsmittels, mit dem sie kristallisieren kann) stabilisiert wird und sich nach Vertreiben dieses zur Tetraamylose polymerisiert, wurde in neuen Untersuchungen noch eingehender belegt. Wir wiesen schärfer als früher nach, dass die beiden Polyamylosen auch in wässriger Lösung so fest mit dem



Alkohol verbunden sind, dass dieser kryoskopisch nicht als selbständiges frei bewegliches Molekül nachweisbar ist. Auch bezüglich der Fähigkeit zur Ausbildung solcher Molekül-Verbindungen unterscheidet sich die Diamylose von der Tetraamylose; die Ausbildung übermolekularer Valenzen ist bei der ersteren wesentlich grösser, so dass sie unter unseren Konzentrationsverhältnissen 8 per cent. Alkohol, die Tetraamylose aber nur 4 per cent, neben ihr kryoskopisch nicht nachweisbaren zu binden vermag. Derartige Erscheinungen, dass in Lösung dispergierte Kolloide durch Verbindung mit artfremden Stoffen in ihrem Teilchen verkleinerten Zustande erhalten bleiben können, dürften häufig anzutreffen sein. Sie müssen für das Verhalten solcher Stoffe im Lösungszustand Bedeutung haben.

BERLIN, 1932.

## **The Report on the Progress of Stereochemistry in India, together with some Relevant Remarks on the Significance of the Doctrine of Symmetry.**

By BAWA KARTAR SINGH.

Among the ideas which have played an important rôle in science, the doctrine of symmetry may certainly be considered as one of the most remarkable and fruitful. Its significance and value for the scientific description of the living and inanimate matter has been recognised from early times.<sup>1</sup>

The idea of symmetry resulted originally from a study of the geometrical forms of natural objects, having some kind of regularity and possessing certain processes of repetition manifested in their external habits.

Natural objects may be grouped under two heads, symmetrical and dissymmetrical. Symmetrical objects may be defined as those which are superposable with their mirror-image. There are other objects which do not fulfil these conditions. These dissymmetric objects are able to exist in two geometrically similar but non-superposable forms, like right and left hands. Such objects are called "opposite" or enantiomorphous, and are characterised by the fact that they do not possess a centre of symmetry, an axis of symmetry, or a plane of symmetry.\*

Dissymmetry should be distinguished clearly from asymmetry, which implies a complete absence of symmetry. Dissymmetry, however, may occur in figures which possess a very high degree of axial symmetry, although it cannot exist in any figure which possesses a plane, a centre, or an alternating axis of symmetry. Thus a dissymmetric crystal of sodium chlorate has 7 axes of symmetry, a crystal of quartz has 4 axes, and even tartaric acid has 1 axis of symmetry, although all other elements of symmetry are lacking in these figures.

The principles and criteria of dissymmetry derived from a study of natural objects, which can be measured by our visual apparatus,

\* The reverse of this proposition is, however, not true. The absence of a centre of symmetry, an axis of symmetry, or a plane of symmetry does not necessarily make an object differ from its mirror image, or give rise to enantiomorphism.

are also found applicable in the case of objects, such as the molecules, the dimensions of which will most probably for ever remain beyond the scope of our direct observation. Thus the phenomenon of enantiomorphism and of enantiomorphous arrangement in space has played an important part in the development of our chemical ideas, and has led to the elucidation of molecular configuration of chemical compounds.

The introduction of the novel idea of molecular dissymmetry into Chemistry by Pasteur<sup>2</sup> was due to his brilliant and epoch-making discovery of a *laevo*-rotatory form of tartaric acid, which was the mirror-image of the ordinary *dextro*-rotatory acid, and led to the creation of the new science of stereochemistry. The history of science has rarely witnessed a discovery that has had such far-reaching consequences in Physics and Chemistry as this one by Pasteur. At the time of this discovery, the theory of Kekulé,<sup>3</sup> based on the quadrivalency of carbon and the law of linking of atoms, had not been advanced, and it was, therefore, not possible for Pasteur to point out more precisely the spatial arrangement of the atoms in the molecule of tartaric acid than by merely indicating some kind of spiral, irregular tetrahedral or enantiomorphous arrangement. The theoretical scheme of Kekulé, however, proved insufficient to embrace all the known facts, which were rapidly growing in number. It was, therefore, no mere matter of chance that in 1874 Van't Hoff<sup>4</sup> and Le Bel<sup>5</sup> independently demonstrated the all-important part which molecular structure in space plays in the interpretation of certain cases of isomerism in Organic Chemistry. They ascribed the optical activity of organic compounds to the presence of one or more asymmetric atoms of carbon. The discovery was overdue, and both of these investigators would have had to yield priority to the Italian Chemist, Paterno,<sup>6</sup> who in 1869 had introduced the idea of a three-dimensional carbon atom, but for the fact that one of the three-dibromoethanes, which he sought to explain by this model, turned out to be non-existent.

During the fifty years which elapsed since the discovery of Pasteur, all attempts to extend the range of optical activity to elements other than carbon ended in failure. It was, therefore, a great experimental triumph, when Pope<sup>7</sup> in 1899, succeeded in preparing an optically active quaternary ammonium base, which owed its rotatory power to an asymmetric atom of nitrogen, instead of to an asymmetric atom of carbon. By the application of newer aids in resolution,

introduced by Pope, in the form of strong, stable, monobasic, optically active sulphonic acids in a non-ionising medium, in place of the weak, aqueous, dibasic acid (tartaric), which had been used hitherto for this purpose, the spell of failure was now broken. As a result of this, numerous optically active compounds, representing at least a score of new types of atomic and molecular dissymmetry, have been prepared. This work has recently been summarised by the writer in his presidential address to the Indian Chemical Society.<sup>8</sup> The resolution of quaternary ammonium compounds was followed by the preparation of another class of optically active nitrogen bases by Meisenheimer,<sup>9</sup> namely, the amine oxides of the general formula  $O:N R_1 R_2 R_3$ . A third class of optically active nitrogen bases was prepared by the present writer<sup>10</sup> in 1913 and in succeeding years. These were the substituted quaternary azonium bases with the general formula,  $N R_1 R_2 R_3 (NH_2)OH$ . These compounds like those of Meisenheimer contained only three organic radicals, the remaining two being inorganic. The rotatory powers of the optically active ions, in aqueous solution, of the different members of the series, together with their formulae and products of asymmetry ( $T$ ), calculated on the tetrahedral configuration of the azonium ion, are given in Table I.

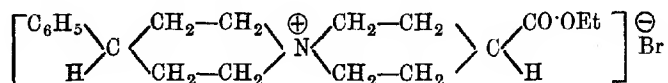
TABLE I.

			$[M]_D$ .	$T \times 10^2$ .
1.	$(C_6H_5)(CH_3)(C_2H_5)(NH_2)N$	...	36°	49.97
2.	$(C_2H_5)(CH_3)(C_7H_7)(NH_2)N$	...	117	48.57
3.	$(C_6H_5)(C_7H_7)(C_3H_5)(NH_2)N$	...	137	222.1
4.	$(C_6H_5)(C_7H_7)(C_3H_7)(NH_2)N$	...	247.5	206.4

One of the objects in preparing the above series of compounds was to test the hypothesis, which Guye<sup>11</sup> put forward in 1890, connecting mass and molecular rotatory power. The degree of molecular dissymmetry was assumed to depend on the differences in mass of the different substituents linked to an asymmetric atom. The product of asymmetry was supposed to determine the magnitude of the rotatory power. The values of the molecular rotatory power and the product of asymmetry given in the table do not support this theory.

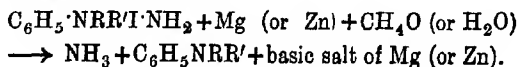
A point of some interest, arising out of the inactivity of the free amino group in the azonium compounds, led the writer in 1913 to put forward the hypothesis "that it is not possible for both the nitrogen atoms to become quinquivalent at the same time owing to steric interference or hindrance."<sup>12</sup> In the light of more recent development

of the electronic theory of valency, it appears to the writer that it would be better to ascribe this inability of the two directly linked nitrogen atoms to become quinquivalent at the same time to electrical influences, rather than to steric hindrance. Since the above-mentioned hypothesis was put forward, the pyramidal configuration of the ammonium and azonium ion has been discarded in favour of the tetrahedral as the result of direct experimental vindication at the hands of Mills and Warren.<sup>13</sup> These investigators prepared a compound which would yield a pair of optically inactive stereoisomers, if the four hydrogen atoms of the ammonium radical were coplanar, whereas, if they were arranged at the corners of a tetrahedron, a pair of optical isomers would be formed. The optical activity of the compound, having the formula



is, therefore, a clear proof of the tetrahedral configuration of the ammonium ion, as contrasted with the alternative pyramidal configuration.

During the course of some unsuccessful attempts to synthesise diammonium type of compounds, the writer developed a new method<sup>12</sup> for the synthesis of tertiary amines as follows: A substituted quaternary azonium haloid with the three suitable alkyl or aryl radicals may be prepared, which on being treated with magnesium (or zinc) in aqueous or methyl alcoholic solution would give the corresponding tertiary amine in quantitative yield, according to the following generalised scheme:



In this way the following tertiary amines were prepared: dimethylaniline, diethylaniline, methylethylaniline, methylpropylaniline, methylbenzylaniline, and propylbenzylaniline. The last base, *viz.*, propylbenzylaniline, was a new substance and was isolated as its picrate.

The other topics of interest, which have been actively studied, may be grouped as follows:

#### I. The Effect of Position Isomerism on Optical Activity.

Frankland<sup>14</sup> put forward his 'lever arm' theory in 1896, stating that the order of rotation in the case of position isomerides was *ortho*

$< \text{unsubstituted compound} < \text{meta} < \text{para}$ . Cohen<sup>15</sup> laid down another rule which is to the effect that the rotatory power produced by an *ortho* substituent differs more from that of the unsubstituted compound than do those of *meta* or *para* derivatives. The writer<sup>16</sup> summarised his views on the subject in 1920 in his presidential address before the Chemical Section of the 7th Indian Science Congress, and has since further shown in several communications<sup>17</sup> that both these rules are invalid.

The conception of a mechanical moment in the 'lever arm' theory of Frankland is replaced in later views on the subject<sup>18</sup> by that of an electrostatic moment. According to this, the influence of a substituent on the optical rotation of a parent compound is dependent in sign and magnitude on the change of the electrostatic moment as suggested by Rule,<sup>19</sup> and will either be of the order  $p > m > o$ , or  $o > m > p$ , and not in the former sequence alone as required by the suggestion of Frankland. The observations of the writer on the rotatory power of the position isomerides of iodo derivatives of phenylaminocamphors<sup>20</sup>, and of anilino- and toluidinomethylenecamphors<sup>21</sup> are at direct variance with these rules. Further the order of the position isomerides on the rotatory power in the same series of compounds changes with the nature of the solvent. This indicates that the correlation of that esoteric property, known as optical activity with the chemical constitution of the molecule is an extremely difficult problem, which must await for its solution till we get from the mathematical physicist a quantitative theory of optical activity.

## II. The Effect of Conjugated Unsaturation on Optical Activity.

Up till the year 1920, *p*-phenylenebisiminocamphor prepared by Forster<sup>22</sup> in 1909, was the classical instance, among carbon compounds, of a substance endowed with the highest rotatory power. The rotation constants of this substance, were subsequently found to be exceeded by two substances, prepared by the writer, namely, 1:4-naphthylenebisiminocamphor<sup>23</sup> and *pp'*-diphenylaminebisaminocamphor.<sup>23a</sup> A study of the structural formulae of the compounds given in Table II brings out in a striking manner the effect of the optimum association of azethenoid groups, conjugated linkings and benzene rings, within a given molecular compass on rotatory power. The narrower the molecular compass containing a given number of conjugated linkings, the greater is the rotation.



The depression in the rotatory power which accompanies the reduction of azethenoid group in the molecule of this class of compounds (Table II) is illustrated in a most striking manner by the values of the rotatory power in pyridine of the six compounds given in Table III.

TABLE III<sup>24</sup>.

Name of substance.	$[M]_{\text{H}_2\text{O}}^{35^\circ}$	Difference.
{ <i>p</i> -Phenylenebisimino- <i>d</i> -camphor (II) ...	8845*	8044*
{ <i>p</i> -Phenylenebisamino- <i>d</i> -camphor ...	301	
{ <i>pp'</i> -Diphenylmethane-bisimino- <i>d</i> -camphor (I) ...	6016	5096
{ <i>pp'</i> -Diphenylmethane-bisamino- <i>d</i> -camphor ...	320	
{ <i>p</i> -Imino- <i>d</i> -camphordiphenylamine (III) ...	8818	8648
{ <i>p</i> -Amino- <i>d</i> -camphordiphenylamine ...	170	

It will be seen that these phenomenal differences in rotatory power effected by such slight changes in molecular weight of these compounds are unknown among optically active substances, and they also far surpass in magnitude any changes in rotatory power in similar types of compounds already known. It also illustrates the very great influence on rotatory power, of conjugated double bonds when situated near the asymmetric centre.

### III. The Influence of Chemical Constitution on the Character of Rotatory Dispersion.

No generalisation in reference to optical rotatory power is likely to give important results, if the substances examined give dispersions of different types. The first object of the work on dispersion is, therefore, to find out the form of the curves, and to classify the different types of rotatory dispersion.

(a) *Classification of Rotatory Dispersion*.—Biot classified rotatory dispersions in two groups, according as they did, or did not obey the law of the inverse squares,  $[\alpha] = k/\lambda^2$ . Recent work has shown that the law is never obeyed exactly, although some substances, such as sodium tartrate<sup>23</sup> and the *dextro* and the *laevo* forms of *p*-iodophenyl-acetylaminocamphor<sup>20</sup>, obey it very nearly. Rotatory dispersions are classified as "simple" and "complex", according as they can, or cannot be expressed by the equation  $[\alpha] = k/\lambda^2 - \lambda_0^2$ . This equation



which differs from Biot's equation only by the addition of  $\lambda_0^2$ , was deduced by Drude in 1898 for rotatory dispersion in transparent media; it therefore does not apply to absorbent media studied by Cotton <sup>26</sup>, where anomalies are observed in passing through the region of absorption.

(b) *Examples of Simple Dispersion.*—The simple dispersion formula of Drude,  $[\alpha] = k/\lambda^2 - \lambda_0^2$  is valid for a large number of secondary alcohols <sup>27</sup> and for nicotine <sup>28</sup>, which contain only one asymmetric carbon atom. It is also valid up to the extreme limits of our present experimental methods for methylcyclohexylidene acetic acid of Perkin, Pope and Wallach <sup>29</sup>, which contains no asymmetric carbon atom. The writer <sup>30</sup>, in collaboration with his pupils has carried out an extended series of determinations on the rotatory dispersion of the *dextro* and *laevo* forms of oxymethylenecamphor, aminomethylenecamphor, and the numerous aryl derivatives of aminomethylenecamphor, and finds that with the solitary exception of *oo'*-dibenzylbisaminocamphors in chloroform solution <sup>31</sup>, they obey the simple dispersion formula. These substances which contain 2 or 4 asymmetric carbon atoms are complex ring-compounds, loaded with double bonds. These and other instances show that the simple dispersion formula can be applied to compounds of varied structure.

(c) *Examples of Complex Dispersion.*—If the rotatory dispersion cannot be expressed by the one-term equation of Drude, it is "complex." This may be *normal* as in the case of camphor <sup>32</sup>, or *anomalous* as in the case of *o'*-bromocamphor <sup>33</sup> and the monoacetyl derivatives of *p*-phenylenebisaminocamphors <sup>34</sup>.

An important application of rotatory dispersion, made by the writer <sup>35</sup>, is in connection with the diagnosis of isomeric, tautomeric and polymeric from polymorphous optically active substances. In the case of polymorphous forms, these values will be identical, whereas these values will be different for isomeric (or tautomeric) modifications.

#### IV. The Physical Identity of Enantiomers.

This subject has been extensively studied in connection with Pasteur's Law in several communications <sup>30, 34</sup> and has been summarised this year by the writer in his presidential address before the Indian Chemical Society<sup>8</sup>.

V. *Optically Active Dyes.*

It is well known that molecular dissymmetry which causes optical activity also causes selective action with living matter and proteins; for example, certain optical antimers are known to have quite different action as drugs, quite different taste and so on. This consideration led the writer to take up the study of optically active camphoreins<sup>36</sup> and other types of optically active dyes<sup>23a</sup>. These are some of the earliest examples of optically active dyes prepared.

VI. *Optical Activity and Phototropy.*

In several communications<sup>37</sup>, the writer has described some camphor derivatives exhibiting phototropism in solution only. These were *a*-naphthylamino-*d*-camphor, *m*-phenylenebisamino-*d*-camphor, and *ar*-tetrahydro-*a*-naphthylamino-*d*-camphor.

The stereoisomeric *a*-naphthylaminocamphors (*d*, *l*, *dl*) exhibit identical phototropic and photochemical changes. The phototropic effect occurs in the following solvents which contain 2 or 3 halogen atoms attached to the same carbon atom: chloroform, bromoform, iodoform (in alcohol), carbon hexachloride (in alcohol), chloral alcoholate and methylene iodide. The exposed solutions react strongly acid to litmus. On the other hand, the effect is not shown in ethylene dibromide, ethyl iodide, methyl iodide, and other ordinary organic solvents. The phototropic colour change and the photochemical oxidation are inhibited by sodium ethoxide as well as by traces of water. Acetylation of the amino group destroys the phototropic effect. Two alternative mechanisms for the phototropic change are advanced; in one of them the solvent is assumed to take part in the change. As limitation of space do not permit any lengthy treatment of topics under (IV), (V) and (VI), it has been found sufficient to enumerate them with very brief comments.

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# Die Verwertung der Kohle auf dem Wege über die Gase.

VON

FRANZ FISCHER.

Ich habe aus dem umfangreichen Gebiet einen Abschnitt ausgewählt, der sich mit der Verwertung der Kohle auf dem Wege über die Gase beschäftigt, und zwar aus zwei Gründen. Erstens halte ich die Verwertung der Kohle auf dem Wege über die Gase für die Zukunft für ein besonders wichtiges Problem und zweitens bin ich in der Lage, durch die in unserem Institut ausgeführten Arbeiten auf diesen Gebiete aus eigener Erfahrung zu sprechen. Das vorliegende Thema habe ich in nachfolgende Abschnitte unterteilt:

- A. Beschaffung der Gase.
- B. Reinigung der Gase.
- C. Verwendung der Gase als solche.
- D. Umwandlung der Gase.

Mit Absicht nicht beschrieben werden in dem Vortrage jene Fälle, bei denen die Kohle lediglich als Quelle für die Beschaffung von Wasserstoff dient, der dann zur Hydrierung von Stickstoff (Ammoniaksynthese) und zur Hydrierung von Ölen, Teeren und Kohlen Verwendung finden soll.

## A. *Beschaffung der Gase.*

Was nun die Beschaffung der Gase angeht, so werde ich zunächst von den in den Kohlen *eingeschlossenen Gasen* erwähnen, dann über die Gase, die durch *Destillation* gewinnbar sind, ferner über die durch *Vergasung* von Kohlen erhältlichen und schliesslich über die durch Umsetzung aus anderen Gasen entstehenden.

Beginnen wir mit den in den Kohlen *eingeschlossenen Gasen*. Wenn diese Gasmengen zumindest im allgemeinen für die Gasbeschaffung auch nicht in Frage kommen, so dürfen sie meiner Ansicht nach in dieser Beziehung nicht unerwähnt bleiben. Denn nicht nur gibt es Kohlen, die auffallend grosse Mengen von Gasen eingeschlossen enthalten, weit mehr als es normalerweise der Fall ist, sondern es gibt auch Kohlen, die anstelle von Methan andere Kohlenwasserstoffe in sich bergen und schliesslich bestehen naturgemäss nahe Beziehungen zwischen den Gaseinschlüssen der Kohlen und den Grubenwettern. Was die Herkunft der in den Kohlen eingeschlossenen Gase angeht, so ist es wohl verfrüht, etwas allgemein Gültiges zu behaupten. Vielleicht ist es so, dass das in den Kohlen enthaltene Methan in ihnen selbst durch chemische und biologische Vorgänge entstanden ist und nicht völlig hat entweichen können, während die anderen in den Kohlen enthaltenen Kohlenwasserstoffe vielleicht von aussen in sie eingedrungen sind und möglicherweise tiefer liegenden Erdöllagerstätten entstammen. Ich glaube, es ist am besten, einstweilen nichts Bestimmtes zu behaupten, sondern die Ergebnisse weiterer Untersuchungen abzuwarten. Dann wird auch die Möglichkeit eintreten, wertvolle andere Schlussfolgerungen zu ziehen, die nicht nur für den Kohlenbergbau, sondern auch für die Erdöltechnik von Bedeutung sind. In der nachfolgenden Tafel I finden Sie Ergebnisse von Untersuchungen, die in unserem Institut in der letzten Zeit über die in den Kohlen vorgebildet eingeschlossenen Gase ausgeführt wurden, und zwar greife ich aus unseren Untersuchungen heraus eine Fettkohle der Zeche Mathias Stinnes, ein Anthrazit aus dem Aachener Revier und eine Fettkohle der Wealdon-Formation aus dem Kohlenbergwerk Minden.

Im Gegensatz zu der Arbeitsweise, die von verschiedenen anderen Forschern bisher auf diesem Gebiete angewendet worden ist, haben wir uns einer selbst konstruierten Mühle bedient, die gestattete, die Gase während des Mahlvorganges bei hohem Vakuum abzupumpen. Die Mühle wurde jeweils mit 100 g. Kohle in Stücken von Nussgrösse beschickt und dann wurde völlig evakuiert und festgestellt, dass in einem längeren Zeitraum kein Gas mehr geliefert wurde. Natürlich war für absolute Dichtigkeit der Mühle gesorgt, und zwar nicht nur bei Stillstand, sondern auch während ihrer Drehung. Die Versuche wurden bei Zimmertemperatur ausgeführt.

TAFEL I.

Kohle.	Streifenkohle (Fettkohle) Zeche Mathr. Stinnes.	Anthrazit Gew. Sophia-Jakoba Aschener Revier.	Fettkohle mit viel Glanzkohle Nr. 5 Kohlenbergwerk Minden.
Beim Mahlen von 100 g. abgepumpte Gasmenge	210 ccm.	890 ccm.	240 ccm.
CO <sub>2</sub>	1·9%	4·2%	2·9%
S. K. W.	0·0	0·0	0·0
CO	0·5	0·5	0·1
H <sub>2</sub>	2·8	4·0	0·0
CH <sub>4</sub>	86·4	90·0	3·8
C <sub>2</sub> H <sub>6</sub>	0·8	0·2	16·8
C <sub>3</sub> H <sub>8</sub>	0·8	—	29·5
C <sub>4</sub> H <sub>10</sub>	—	—	41·7
C <sub>5</sub> H <sub>12</sub>	—	—	1·8
C <sub>6</sub> H <sub>14</sub>	—	—	1·4
N <sub>2</sub>	7·2	1·1	2·0
Flüssige Kohlenwasser- stoffe			0·3 ccm

Die Betrachtung der vorstehenden Tafel zeigt, dass die *Ruhrkohle* 210 ccm Gas abgab, welches im wesentlichen aus Methan bestand, höhere Homologe des Methans waren weniger als 1% vorhanden.

4·5mal soviel Gas gab der *Anthrazit* der Gewerkschaft Sophia-Jakoba, und zwar bestand das Gas wiederum im wesentlichen nur aus Methan. Die scheinbare Dichte dieses Anthrazits wurde zu 1·41 ermittelt, hieraus ergibt sich ein spezifisches Volumen von 0·71.100 g. des verwendeten Anthrazits hatten also ein Volumen von 71 ccm. Wäre der Raum von 71 ccm nicht mit Anthrazit erfüllt gewesen, so hätten die während der Vermahlung entbundenen 900 ccm Gas in diesem Raum bereits nur bei einem Druck von 14 Atm. untergebracht werden können. Nun war aber der Raum nicht leer, sondern von Anthrazit erfüllt, dementsprechend muss der Druck des Gases in der Kohle noch viel höher als 14 Atm. gewesen sein. Würde

man ein Porenvolumen von 10 per cent annehmen, so würde sich bereits ein Druck von 130 Atm. berechnen. Der Umstand, dass das in dem Anthrazit enthaltene Gas aus nussgrossen Stücken zum mindesten mit ausserordentlicher Langsamkeit entweicht, lässt darauf schliessen, dass das Gas in der Kohle in winzigen Hohlräumen eingeschlossen ist, die untereinander so gut wie keine Verbindung haben. Dass das Gas in diesen Hohlräumen adsorbiert ist, dagegen spricht der Umstand, dass es bei Freilegung der Hohlräume, welche beim Vermahlen bis auf eine Teilchengrösse in der Nähe von  $1\mu$  stattfindet, im Vakuum entweicht.

Die Gasausbeute beim Vermahlen der Kohle des Kohlenbergwerks Minden ist ungefähr von derselben Grösse wie bei der schon beschriebenen Ruhrkohle. Aber die Analyse des entbundenen Gases zeigt, dass es sich hier nicht um Methan sondern fast ausschliesslich um höhere Homologe desselben handelt. Durch Ausfrieren des entbundenen Gases mit flüssiger Luft wurden sogar noch flüssige Kohlenwasserstoffe ausgeschieden in der Grössenordnung von 0.8 ccm auf 100 g Kohle.

Diese Untersuchungen, an denen die Herren *Peters* und *Warnecke* beteiligt sind, werden noch auf andere Kohlen ausgedehnt werden und hierüber wird in einer besonderen Mitteilung berichtet werden. Wenn auch, wie ich schon sagte, im allgemeinen die in den Kohlen vorgebildet enthaltenen Gase als Gasquelle nur unter besonderen Umständen in Frage kommen dürften, so glaubte ich doch, über diese interessanten Ergebnisse hier etwas sagen zu sollen.

Ich komme nun zu der *Beschaffung der Gase* auf dem Wege über die *Verkokung*. Die nachstehende Tafel II weist darauf hin, inwieweit die bei der Verkokung entstehenden Gase hinsichtlich ihrer Zusammensetzung variiert werden können. Was zunächst das durch Destillation bei niedriger Temperatur entstehende, sogenannte Schmelgas angeht, so ist es relativ arm an Wasserstoff aber reich an Methan und höheren Kohlenwasserstoffen. Die Menge beträgt zwischen 50 und 100 cbm/t Kohle.

TAFEL II.

(a) Urgas	Arm an $H_2$ , reich an s.K.W.,
(b) Kokereigas	mehr als 50% $H_2$ , 5-6% CO, 25% $CH_4$ ,
(c) Anfangkokereigas	arm an $H_2$ ,
(d) Endkokereigas	reich an $H_2$ ,
(e) Wassergashaltiges Kokereigas	reicher an CO.

Erheblich grösser ist bekanntermassen die Menge des Kokereigas, etwa 300 cbm/t Kohle. Sein Wasserstoffgehalt beträgt im Gegensatz zum Urgas über 50 per cent, daneben finden sich, was im Rahmen des Vortrages vorwiegend interessiert, 5-6 per cent. Kohlenoxyd und etwa 25 per cent Methan. An und für sich wäre es möglich, was aber praktisch im Kokereibetrieb kaum durchführbar ist, sowohl wasserstoffarmes als auch wasserstoffreiches Gas bei der Kokerei zu erzeugen, denn das am Anfang des Verkokungsvorganges entstehende Gas ist ärmer an Wasserstoff und das gegen Ende der Gasungszeit entwickelte enthält wohl mehr Wasserstoff, als das normale Kokereigas. Für viele Zwecke wäre wohl ein wassergashaltiges Kokereigas von Vorteil. Versuche nach dieser Richtung sind schon mehrfach gemacht worden. In den letzten Jahren sind von verschiedenen Seiten Wege empfohlen worden, durch Einführen von Dampf gegen Ende der Verkokung die Gasausbeute zu vermehren, was durch Reaktion des Wasserdampfes mit dem glühenden Koks stattfindet. Da sich hierbei Wassergas mit annähernd gleichen Teilen Wasserstoff und Kohlenoxyd bildet, so steigt dadurch der prozentische Gehalt des Kokereigas an Kohlenoxyd. Die aus Kohlen durch Verkokung entstehenden Gase haben für die Verwertung der Kohle auf dem Wege über die Gase Bedeutung, einerseits durch ihren Gehalt an Kohlenoxyd und Wasserstoff, andererseits durch ihren Gehalt an Methan bzw. auch höheren Kohlenwasserstoffen.

Eine umfangreiche Quelle für die Beschaffung von Gasen bildet die *Vergasung der Kohle*, und zwar für alle diejenigen Verfahren, bei denen der Gehalt der Gase an Kohlenoxyd und Wasserstoff wichtig ist. Während man bei der Verwendung von Verkokungsgasen an den Absatz des Hauptproduktes der Verkokung gebunden ist, ist man bei Synthesen, welche die durch Vergasung gewinnbaren Gase benutzen, weitgehend unabhängig. Auf diesem Wege kann man die ganze Kohle in synthetische Produkte umwandeln. Die nachstehende Tafel III gibt einen Überblick über die durch Vergasung gewinnbaren Gasarten.

TAFEL III.

- (a) Luftgas } gegen 30% CO
- (b) Gichtgas }
- (c) Wassergas (Einfluss der Temperatur) 40–50% CO, 50–55% H<sub>2</sub>. Diskontinuierlich, drei kontinuierl. Wege (O<sub>2</sub> + Dampf, O<sub>2</sub> + CO<sub>2</sub>, ferner Stassano, Hillebrand).
- (d) Generatorgas 28% CO, 11% H<sub>2</sub>
- (e) besonders CO-reiches Wassergas, besonders H<sub>2</sub>-reiches Wassergas.



Luftgas und Gichtgas mit einem Kohlenoxydgehalt von etwa 30% kommen für sich allein als Ausgangsstoffe nicht in Frage, wohl aber als Zumischung zu wasserstoff-reichen Gasen um deren Kohlenoxyd-gehalt zu erhöhen. Wassergas, das je nach den Temperaturbedingungen in seiner Zusammensetzung sich dem theoretischen Wert von gleichen Teilen Kohlenoxyd und Wasserstoff nähert oder bei niedrigerer Temperatur wachsende Mengen von Kohlensäure und einen dementsprechend höheren Wasserstoffgehalt als 50 per cent. aufweist, ist von wachsender Wichtigkeit für synthetische Zwecke. Seine Herstellung geschieht bisher in der Hauptsache diskontinuierlich und ist durch das abwechselnde Heissblasen und Gasen mit beträchtlichen Wärmeverlusten verbunden. Man ist schon seit längerer Zeit bestrebt, die Wassergasherstellung auf kontinuierlichem Weg auszuführen, indem man die für die endotherme Wassergasbildung notwendige Wärme auf anderem Wege als durch das Heissblasen mit Luft beschafft. Wege hierzu bietet die elektrische Heizung der Kokssäule nach *Stassano* oder die Vorheizung des Wasserdampfes durch den elektrischen Lichtbogen nahe an 2000°, ferner das *Hillebrand*'sche Verfahren, in welchem hoch erhitztes Wassergas mit wenig Dampf mit dem Koks in Berührung gebracht wird. Eine andere Möglichkeit, die aber nicht zu dem üblichen Wassergas, sondern zu einem kohlenoxydreicherem Gas führt, ist die Vergasung mit einem Gemisch von Sauerstoff und Dampf. Hierüber ist in den letzten Jahren von *Parr* und *Drawe* gearbeitet worden. Die Herstellung von Generatorgas durch Vergasung mit einem Dampf-Luft-Gemisch lässt sich, wie bekannt, zwar kontinuierlich gestalten, liefert aber ein stickstoffreiches Gas, welches beispielsweise 28% Kohlenoxyd und 11% Wasserstoff enthält.

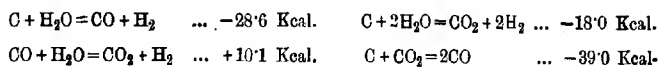
Man erkennt aus vorstehenden Ausführungen, dass es möglich ist, auf dem Wege über die Vergasung direkt für synthetische Zwecke brauchbare Gasgemische zu erzeugen und dass man auch deren Kohlenoxyd-Wasserstoffverhältnis variieren kann. Kohlenoxydreiches Gas kann man auch durch Vergasung mit Sauerstoff + Dampf, wasserstoffreiches Gas durch die übliche Wassergasherstellung bei niedrigerer Temperatur und Auswaschung der Kohlensäure herstellen. Im übrigen können die verschiedenen Gasgemische durch geeignetes Vermischen der bisher erwähnten Gase erzeugt werden.

Für die Verwertung der Kohle auf dem Wege über die Gase wird für die Zukunft die Ausbildung von Grossgeneratoren, vielleicht

ähnlich dem *Winkler-Generator* der I. G. Farbenindustrie A. G., von wachsender Bedeutung sein. Die konstruktiven Schwierigkeiten werden sich überwinden lassen, wenn auch wahrscheinlich für die verschiedenen Kohlearten oder Koksarten je nach Korngrösse, Backvermögen u. dgl. verschiedene Konstruktionen ausgebildet werden müssen.

Die der Vergasung des Kokses zugrunde liegenden Reaktionen sind in *Tafel IV* zusammengestellt.

TAFEL IV.



Wir sehen, dass sie alle endotherm sind. Den geringsten Energieaufwand erfordert die Vergasung zu Kohlensäure und Wasserstoff. Die Umsetzung des Kohlenoxyds mit Wasserdampf zu Kohlensäure und Wasserstoff selbst ist eine exotherme Reaktion. Bei dieser Gelegenheit möchte ich an die Versuche erinnern, mit denen man die Geschwindigkeit der Wassergasbildung auf katalytischem Wege zu beeinflussen versucht hat. Cobb und Marson haben gezeigt, dass durch Alkalicarbonate und andere basische Zusätze die Geschwindigkeit bei niederen Temperaturen wesentlich erhöht wird. Versuche aus unserem Institut haben ergeben, dass die unter Volumausdehnung stattfindende Einwirkung der Kohlensäure auf Kohlenstoff durch verminderten Druck stark begünstigt wird, so wie es die Theorie verlangt. Häufig sind die erhältlichen Gase nicht von der Zusammensetzung, wie sie für synthetische Zwecke benötigt werden und können auch nicht durch Zumischung auf die gewünschte Zusammensetzung gebracht werden. In solchen Fällen kann man sich der Umsetzung von Gasen mit Dampf oder mit Kohlensäure oder mit beiden bedienen. Nachstehende *Tafel V* gibt die theoretisch erhältlichen Werte von Umsetzungsgasen, wenn man von Kokereigas mit einen Gehalt von 25% Methan ausgeht.

TAFEL V.

- (a) Umsetzung von Kokereigas mit Dampf bei 1000° an Nickel: aus 1 cbm Kokereigas 1.8 cbm Spaltgas mit 18% CO und 73% H<sub>2</sub>.
- (b) Umsetzung von Kokereigas mit O<sub>2</sub> (partielle Verbrennung): aus 1 cbm Kokereigas 1.5 cbm Spaltgas mit 22% CO und 68% H<sub>2</sub>.
- (c) Umsetzung von Kokereigas mit CO<sub>2</sub> bei 1000° an Nickel: aus 1 cbm Kokereigas 1.8 cbm Spaltgas mit 39% CO und 58% H<sub>2</sub>.

Hierdurch besteht ein Weg, beispielsweise vom Kokereigas ausgehend, Kohlenoxyd-Wasserstoffgemische zu erzeugen, welche statt nur 5% Kohlenoxyd wie im Kokereigas je nach Wunsch Kohlenoxydgehalte zwischen 18 und 39% haben. Wünscht man ein Gas, das genau doppelt so viel Wasserstoff wie Kohlenoxyd enthält, so ist diese Zusammensetzung leicht zu erhalten, wenn man das Kokereigas mit einem berechneten Gemisch von Wasserdampf und Kohlensäure umsetzt. Um den Abschnitt über die Beschaffung der Gase zu vervollständigen, sei noch auf Tafel VI verwiesen, welche die Wege angibt, auf denen Gase beschafft werden können, deren Wert für die weitere Synthese in ihrem Methangehalt beruht.

#### TAFEL VI.

##### *Methan und methanreiche Gase.*

- (a) Durch Fraktionierung von Kokereigas nach Linde.
- (b) Durch Katalyse aus CO oder  $\text{CO}_2 + \text{H}_2$  oder aus Kokereigas, Kokereigas + Wassergas u. dgl. mehr.

Bei der Fraktionierung von Kokereigas nach Linde, so wie sie für Zwecke der Ammoniaksynthese vorgenommen wird, füllt ein methanreiches Restgas an, dass für die Ammoniaksynthese nicht benötigt wird aber für viele synthetische Zwecke von Wert ist. Es mag auch Gegenden und Fälle geben, wo das notwendige Methan auf anderen Wegen beschafft werden muss, dann besteht die Möglichkeit, es synthetisch nach Sabatier aus Gemischen von Kohlenoxyd und Wasserstoff oder Kohlensäure und Wasserstoff oder aus Kokereigas + Wassergas zu erzeugen.

##### *B. Reinigung der Gase.*

Ein kurzer Abschnitt sei der Reinigung der Gase gewidmet. Die mechanische Reinigung und die elektrische Reinigung (vgl. Tafel VII) dienen der Entstaubung und der Entleerung von Gasen und müssen unter allen Umständen vorgenommen werden. Für fast alle Zwecke, abgesehen von der direkten Verfeuerung, ist auch eine chemische Reinigung vonnöten, die sich hauptsächlich auf die Entfernung des Schwefelwasserstoffs erstreckt. Hierzu bedient man sich der festen Gasreinigungsmasse, die bisher trotz

## TAFEL VII.

- |  |   |                             |
|--|---|-----------------------------|
| (1) Mechanische Reinigung                      | } | Entstaubung und Entteerung. |
| 2) Elektr. Reinigung                           |   |                             |
| (3) Chem. Reinigung, insbesondere von $H_2S$ : |   |                             |
| (a) feste Gasreinigungsmasse,                  |   |                             |
| (b) Waschung.                                  |   |                             |
| (4) Trocknung, Befreiung von Naphthalin usw.   |   |                             |
| (5) Reinigung von org. S-Verbindungen.         |   |                             |

vieler Vorschläge durch andere Verfahren nur ganz gelegentlich hat verdrängt werden können. So wird die Gasreinigung durch Waschen der Gase mit Waschflüssigkeiten in Türmen einstweilen nur an wenigen Stellen ausgeführt. Sogar neuere Anlage bedienen sich wieder der festen Gasreinigungsmasse. Insbesondere für Zwecke der Fernleitung von Gasen ist auch noch eine Trocknung und Befreiung von Naphthalin notwendig. Auf diesem Gebiete sind in der letzten Zeit beträchtliche Fortschritte gemacht worden.

Für die meisten Fälle, bei denen die Gase katalytischen Verfahren unterworfen werden sollen, reicht die Befreiung der Gase von *Schwefelwasserstoff* als Reinigungsmassnahme nicht aus. Bei der Verwendung von nicht giftfesten Katalysatoren—und für viele Reaktionen, die sich bei niederen Temperaturen abspielen müssen, sind giftfeste Katalysatoren noch nicht bekannt—müssen auch die *organischen Schwefelverbindungen* des Gases weitgehend entfernt werden, da sonst die Katalysatoren vergiftet und in kurzer Zeit unbrauchbar werden. Eine Reinigung der Gase von organischen Schwefelverbindungen bis zu einem Gehalt von 0.2 g Schwefel/100 cbm ist auf Grund der Erfahrungen der letzten Jahre heute leicht möglich. Während diese Reinigung notwendig ist bei der katalytischen Umwandlung von Kohlenoxyd oder Kohlensäure mit Wasserstoff und Katalysatoren der Eisengruppe, ist sie nicht nötig vor rein thermischen oder elektrischen Umwandlungsreaktionen.

## C. Verwendung der Gase als solche.

Bei einem Bericht über die Verwertung der Kohle auf dem Wege über die Gase braucht wohl auf die Verwendung der Gase als solche nicht weiter eingegangen zu werden. Dass sie hauptsächlich zur Beheizung billiger Art und zur Krafterzeugung dienen, ist jedermann

bekannt. Aber es darf wohl darauf hingewiesen werden, dass Gase mit erhöhtem Heizwert vielleicht später als Ferngas in Frage kommen, da die Ausnutzung der Ferngasleitungen mit Gasen von hohem Heizwert naturgemäss eine bessere ist. Je länger die Ferngasleitungen werden, desto wichtiger wird es sein, Gase mit möglichst hohem Heizwert zu transportieren. Die amerikanischen Ferngasleitung von *Texas* nach *Chicago*, die ich Ende des letzten Jahres gesehen habe und die eine Länge hat, die der Entfernung von *Venedig* nach *Kiel* entspricht, wäre völlig unwirtschaftlich, wenn man darin etwa Kokereigas versenden wollte, geschweige denn noch weniger heizkräftige Gase. Aber selbst beim Transport des Methans, das ungefähr den doppelten Heizwert hat, erhöhen sich die Kosten von 5 cent für 1,000 Kubikfuss in Texas auf 50 cent/1000 Kubikfuss am Ende der Leitung in Chicago.

#### D. Umwandlung der Gase.

Nachdem nun die Beschaffung und die Reinigung der Gase und ihre Verwendung als solche besprochen sind, komme ich nun zu der Umwandlung der Gase. Die hierzu in Frage kommenden Verfahren lassen sich einteilen in *katalytische* Verfahren, in *elektrische* Verfahren, in *thermische* Verfahren und schliesslich *biologische* Verfahren. Die katalytischen Verfahren wiederum kann man, wie aus Tafel VIII ersichtlich, einteilen in *Normal drucksynthesen*, d. h. in solche, die bei gewöhnlichem Druck ausführbar sind bzw. ausgeführt werden müssen und *Hochdrucksynthesen*, welche nur bei hohen Drucken durchführbar sind.

### TAFEL VIII.

#### 1. Katalytische Verfahren.

##### Normaldrucksynthesen.

- (a) Methan nach Sabatier aus  $\text{CO} + 3 \text{H}_2$  oder aus  $\text{CO}_2 + 4 \text{H}_2$ .
  - (b) Benzin und Paraffin nach Franz Fischer und Tropsch aus  $\text{CO} + \text{H}_2$ .
- ##### Hochdrucksynthesen.
- (c) Methylalkohol nach I. G. Farbenindustrie A. G., bzw. Angaben von Patart.
  - (d) Syntbol nach Franz Fischer und Tropsch.

Zu den Normaldrucksynthesen gehört die bekannte *Synthese des Methans* nach Sabatier aus Kohlenoxyd und Wasserstoff oder aus Kohlensäure und Wasserstoff. Diese Synthese kann bei gewöhnli-

chem Druck aber auch bei erhöhtem Druck mit Katalysatoren der Eisengruppe, am besten mit Nickel, ausgeführt werden. Während die Synthese von Sabatier wohl *nur* ausnahmsweise im Hinblick auf die Verwertung der Kohle praktische Bedeutung haben wird, kommt die von *Franz Fischer* und *Tropsch* gefundene *Benzinsynthese* aus Kohlenoxyd und Wasserstoff einem dringenden Bedürfnis entgegen. Sie liefert sämtliche Kohlenwasserstoffe der Methanreihe vom Methan aufwärts bis zu über 100° schmelzendem festem Paraffin, also alle Produkte, die man mit den Namen *Gasol*, *Benzin*, *Petroleum* und *Gasöl* bezeichnet. Durch jahrelange Untersuchungen ist es gelungen, die Synthese so zu leiten, dass vorzugsweise die besonders erwünschten Produkte, nämlich Benzin und Öle entstehen. Diese Synthese verläuft am besten bei Atmosphärendruck. Geht man zu höheren Drucken über, so entstehen andere Produkte, und zwar nicht mehr Kohlenwasserstoffe sondern sauerstoffhaltige Produkte. Als Katalysatoren dienen, ebenso wie bei der Methansynthese, Metalle der Eisengruppe. Als Katalysator ist Kobalt vielleicht etwas besser als Nickel. Nickel ist aber wegen seines niedrigeren Preises für praktische Zwecke wahrscheinlich vorteilhafter. Für die Benzinsynthese müssen sehr viel reaktionsfähigere Kontakte verwendet werden als für die Methansynthese, denn man muss bei Temperaturen arbeiten, die unter dem Optimum für die Methanbildung liegen. Erwähnt sei hier noch, dass, während die Methansynthese sich sowohl mit Gemischen von Kohlenoxyd und Wasserstoff als auch mit Gemischen aus Kohlensäure und Wasserstoff ausführen lässt, die Benzinsynthese bisher nur mit Kohlenoxyd + Wasserstoff gelingt. Mit Kohlensäure ist sie nur auf dem Wege über das Kohlenoxyd durchführbar.

Im Gegensatz zu den Normaldrucksynthesen stehen, wie schon erwähnt, die Hochdrucksynthesen. Mit Zinkoxyd als Katalysator wird bei einer Temperatur von über 300° und Drucken von mindestens 160 Atm. aus einem entsprechenden Gasgemisch  $1 \text{ CO} + 2 \text{ H}_2$  Methylalkohol gewonnen. Das Verfahren wird im grossen Massstab von der I. G. Farbenindustrie A. G. ausgeführt. Die ersten Angaben in der Literatur stammen von Patart (*Compt. rend.*, 1924, 179, 1930). In der Zwischenzeit sind zahlreiche Untersuchungen über die Herstellung von Methylalkohol erschienen und auch andere Katalysatorzusammensetzungen angegeben worden, bei denen Kupfer und Chrom eine besondere Rolle spielen. Die Gegenwart von Metallen der Eisengruppe muss bei der Synthese des Methylalkohols vermieden werden.

Im Gegensatz hierzu haben Franz Fischer und Tropsch ein Verfahren beschrieben, nach welchem im wesentlichen andere sauerstoffhaltige Produkte als Methylalkohol, nämlich höhere Alkohole, Aldehyde und Ketone sowie Säuren entstehen. Als Katalysator dienten dabei alkalisierte Eisenspäne. Dieses komplexe Gemisch wurde aus praktischen Gründen "*Synthol*" genannt. Die hierzu verwendeten Temperaturen und Drücke sind 400-450° und 150 Atm. Während man also bei den Normaldrucksynthesen je nach den Arbeitsbedingungen entweder Methan oder die höheren Glieder der Paraffinreihe herstellen kann, kann man bei den Hochdrucksynthesen je nach den Arbeitsbedingungen entweder Methylalkohol oder vorzugsweise höhere Alkohole im Gemisch mit anderen sauerstoffhaltigen Produkten gewinnen.

Zu dem Kapitel katalytische Verfahren muss noch die Herstellung von Kohlenstoff aus Kohlenoxyd erwähnt werden, ein Verfahren, welches sich sowohl bei gewöhnlichem als auch erhöhtem Druck durchführen lässt bei Temperaturen zwischen 400 und 500° am zweckmässigsten mit Eisen als Kontakt. Wenige Prozente von Eisen sind in dem gewonnenen Kohlenstoff enthalten, aber leicht daraus zu entfernen. Erwähnt sei noch, dass dieses Verfahren, wenn es bei niedriger Temperatur ausgeführt wird, sowohl schwefelfreies Kontakte als auch schwefelfreies Gas erfordert.

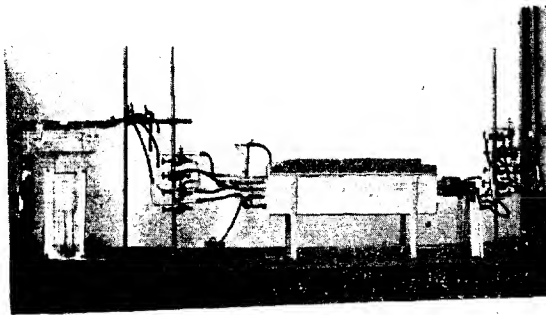
Ich möchte nun zunächst auf die *Benzinsynthese* eingehen und verweise hinsichtlich der Zusammensetzung der Kontakte auf die anschliessende Tafel IX.

TAFEL IX.

Eisen	Kobalt	Nickel	Bemerkungen
Eisen Kupfer	Kobalt Zink		Durch Zersetzung
Eisen Kupfer Natrium Alu- minat	Kobalt Kupfer		der Nitrate in der Hitze
	Kobalt Kupfer Mangan		
	Kobalt Kupfer Thorium		
	Kobalt Mangan Kieselgur	Nickel Thorium Kieselgur	Cu-frei, gefällt mit Kaliumcar- bonat und ge- trocknet
	Kobalt Thorium Kieselgur	Nickel Mangan Kieselgur	

Nachdem wir anfangs gefunden hatten, dass die katalytische Wirkung von Eisen und Kobalt durch Kupfer gewaltig gesteigert werden konnte, fanden wir später weitere Zusätze, die sich als vorteilhaft erwiesen, nämlich bei den Eisenkontakten Natrium-Aluminat, bei den Kobaltkontakten Mangan und Thorium. Allgemein wurde beobachtet, dass, je niedrigerer die Temperatur war, bei der gearbeitet werden konnte, umso grösser die Ausbeuten an flüssigen Kohlenwasserstoffen wurden und dass Alkalizusatz zu den Kontakten, insbesondere starke Alkalien, die Bildung festen Paraffins begünstigten. Alle diese Kontakte von Eisen und Kobalt waren durch Zersetzung der Gemische der Nitrats in der Hitze zunächst in Form von Oxyden gewonnen worden. Es erwies sich als unmöglich, mit Nickel in der gleichen Weise zu verfahren und entsprechende Nickel-Kupferkontakte herzustellen. Der Kupferzusatz, der für Eisen und Kobalt vorteilhaft ist, macht Nickel inaktiv. Vermutlich beruht es darauf, dass im Gegensatz zu Eisen und Kobalt Nickel und Kupfer unbeschränkt löslich sind, wodurch reines Nickel im Kontakt überhaupt nicht mehr vorhanden ist. Zu brauchbaren Nickelkontakten gelangten wir erst dann, als wir auf das Kupfer verzichteten und dazu übergingen, die Nitrats in Gegenwart von Thorium oder Mangan und in Gegenwart von Kieselgur mit Kaliumcarbonat zu fällen und diese Kontakte nur noch trockneten, statt sie in Oxyde überzuführen. Mit diesen Reaktionsfähigen Kontakten kann nun unter 200° gearbeitet werden und dementsprechend werden nunmehr grosse Ausbeuten an flüssigen Produkten erhalten. Die für die Laboratoriumsversuche benutzte Apparatur zeigt Abbildung 1.

ABB 1.



Für die Ausführung der Tausende von Kontaktprüfungen haben wir eine grössere Zahl solcher Öfen in Betrieb, und jeder Ofen gestat-



tet wiederum, gleichzeitig 4 Kontakte zu untersuchen. Ein solcher Ofen besteht aus einem zylindrischen Aluminiumblock, der 4 Längsbohrungen enthält, in welche die Kontaktrohre eingeschoben werden. Er ist mit Diatomitsteinen umgeben und mit einer äusserst genau arbeitenden Temperaturregulierung versehen. Gewöhnlich wird in ein Rohr ein schon bekannter Kontakt gebracht und in die drei anderen Rohre werden Varianten dieses Kontaktes gegeben, damit man sicher ist, dass alle vier Kontakte exakt genau dieselbe Temperaturbehandlung erfahren. Vor jedem Kontaktrohr befindet sich ein Strömungsmesser und hinter jedem Rohr ein Auffangegefäss für diejenigen Kohlenwasserstoffe, die sich bei Zimmertemperatur aus dem Gas von selbst abscheiden, der Rest der leichten flüssigen Kohlenwasserstoffe wird jeweils mit aktiver Kohle herausgenommen. Die kupferhaltigen Kontakte konnten jeweils direkt mit dem Synthesegas, bestehend aus einem Teil Kohlenoxyd und etwas mehr als 2 Teilen Wasserstoff, bei der Synthesetemperatur in Betrieb genommen werden. Die kupferfreien Kontakte werden zweckmässigerweise vorher bei höherer Temperatur mit Wasserstoff reduziert.

Was nun das Mengenverhältnis der gebildeten Kohlenwasserstoffe in Prozenten des verbrauchten Kohlenoxyds angeht, so ist das Nähere darüber aus Tafel X zu erschen.

#### TAFEL X.

##### *Mengenverhältnis der gebildeten Kohlenwasserstoffe in % des verbrauchten CO.*

17·5 % Methan, Athan, Gasöl.  
 55 % Benzin, bis 220° siedend.  
 25 % Öl, von 220° siedend.  
 1·5 % Paraffin, im Kontakt.

Man sieht, dass mit einem guten Kobaltkontakt bis zu 55% des verbrauchten CO als Benzin erhalten werden und 26% als Öle. Es ist durchaus wahrscheinlich, dass im Laufe der Zeit auf empirischem Wege noch weitere Bedingungen gefunden werden, unter denen sich die Bildung von Benzin auf Kosten der anderen Produkte noch höher treiben lässt. Bedauerlicherweise ist man hierbei auf reine Empirie angewiesen, theoretische Fingerzeige sind so gut wie nicht vorhanden.

Die einstweilen weniger erwünschten Produkte sind 17·5% Methan, Athan und Gasöl (Gasöl = Propan + Butan) und andererseits

hochsiedendes, festes Paraffin, von welchem das niedriger siedende in den Ölen gelöst ist, während das hochsiedende sich im Kontakt anreichert. Wir haben Paraffinkerzen, die aus derartigem synthetischen Paraffin hergestellt sind. Sie sind also auf dem Wege über den Koks und das Kohlenoxyd entstanden.

In Tafel XI sind einige konstruktive Grundsätze für die Benzinsynthese und die Gründe dafür zusammengestellt.

#### TAFEL XI.

##### *Konstruktive Grundsätze für die Durchführung der Benzinsynthese.*

Gasverteilung über Kontakt.

Gleichmässigkeit der Temperatur z. B. von  $200^{\circ} \pm 5^{\circ}$ .

Wärmeabfuhr bei dieser Temperatur, d. h. unter Konstanthaltung der  $200^{\circ}$ .

Wärmemenge, die bei der Reaktion erzeugt wird: ca. 20% der Verbrennungswärme der Gase. Bei einer spez. Wärme von 0.3 bedeutet das eine Erhitzung um ca.  $1500^{\circ}$ .

Raumgeschwindigkeit ca. 100 (Maschinenhalle!).

Erschwerung gegenüber der  $\text{NH}_3$ -Synthese, da bei zu hoher Temperatur die Reaktion andere irreversible Bahnen einschlägt, nicht aber einfach die Ausgangsstoffe zurückbildet.

Suspension des Kontaktes in Öl. Zu langsam, aber neue Wege.

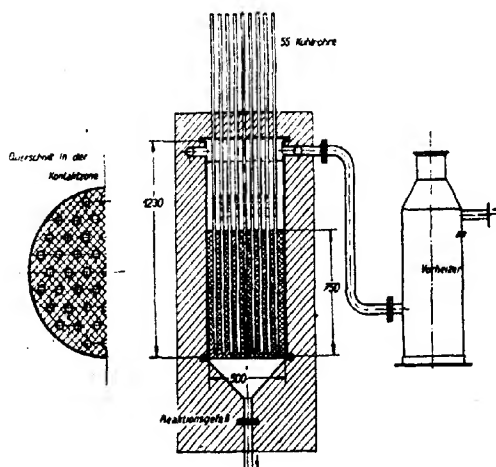
Dazu ist folgendes zu bemerken. Bei grossen Apparaten, wenn also mit grossen Kontaktquerschnitten gearbeitet wird, muss, um optimale Ausbeuten zu erhalten, für eine sehr gute Gasverteilung über dem Kontakt Sorge getragen werden. Während dieser Gesichtspunkt schliesslich für alle katalytischen Verfahren gilt, stellt aber die Benzinsynthese besondere Anforderungen hinsichtlich der exakten Einhaltung der Reaktionstemperatur. Bei Verwendung von Nickelkontakten, wie wir sie in der letzten Zeit benutzen, ist in der ganzen Kontaktapparatur eine gleichmässige Temperatur von  $200^{\circ} \pm 5^{\circ}$  erforderlich. Ist schon die Einhaltung einer derartigen Temperaturgleichheit bei Reaktionen, die ohne grosse Wärmeentwicklung verlaufen, nicht ganz einfach, so wächst diese Schwierigkeit durch die grosse Wärmemenge, die bei der Reaktion erzeugt wird und abgeführt werden muss.

Die Bildung von Benzin und Wasser aus Kohlenoxyd und Wasserstoff erzeugt eine Wärmemenge, die annähernd gleich ist 20% der Verbrennungswärme des in Reaktion tretenden Gasgemisches. Bedenkt man, dass die spezifische Wärme des zur Anwendung kommenden Mischgases etwa 0.3 beträgt, so müsste, wenn keine andere

Möglichkeit der Ableitung der Reaktionswärme bestünde, das Gas selbst um  $1500^{\circ}$ , wenigstens lokal, erhitzt werden. D. h. mit anderen Worten, die Reaktion würde rückläufig oder käme garnicht zustande. Aber schon wenn die Wärmeabführung nicht ganz ausgezeichnet ist, bilden sich andere Produkte als das erstrebte Benzin. Bei einer Steigerung der Temperatur bis gegen  $300^{\circ}$  entsteht nur noch Methan und bei noch höherer Temperatur wird Kohlenstoff abgeschieden. In beiden Fällen ist eine entsprechende Gasmenge für die Benzinsynthese verloren. Vergleicht man damit die Verhältnisse bei der Bildung der Kontaktschwefelsäure aus  $\text{SO}_2$  und Sauerstoff oder bei der Ammoniaksynthese aus Stickstoff und Wasserstoff, so erkennt man die geringere Schwierigkeit bei diesen beiden Verfahren ohne weiteres. Steigt bei diesen Verfahren die Temperatur zu hoch, so bilden sich die Ausgangsstoffe zurück, um sich nachher an einer kühleren Stelle wieder zu vereinigen. Die Vermeidung irreversibler unerwünschter Reaktionen bei der Benzinsynthese hat deshalb besondere konstruktive Grundsätze als notwendig erkennen lassen, eine Frage, die aber heute als gelöst betrachtet werden darf.

Der Umstand, dass bei relativ niedriger Temperatur gearbeitet werden muss, führt dazu, dass die Raumgeschwindigkeit der Benzinsynthese sich einstweilen nur in der Nähe von 100 bewegt, denn sonst wäre es nicht möglich, die Reaktionswärme abzuführen und die Temperatur konstant zu halten. Im übrigen sei darauf hingewiesen,

ABB. 2.



dass man sich von den scheinbar hohen Raumgeschwindigkeiten bei Hochdruckverfahren, wie z. B. bei der Ammoniaksynthese, nicht blenden lassen darf. Zu den scheinbar kleinen Hochdruckkontakttrohren muss in Wirklichkeit noch die Grosse Maschinenhalle zugerechnet werden, in der sich die Hochdruckkompression befindet.

Wir haben natürlich auch versucht, die gleichmässige Temperatur des Kontaktes dadurch zu gewährleisten, dass wir ihn ähnlich wie bei der Fetthärtung in Öl suspendierten. In der Tat lässt sich auf diesem Wege die Reaktion durchführen, aber die Raumgeschwindigkeit wurde dadurch nicht grösser, dagegen ist ein erheblicher Kraftaufwand erforderlich.

Von den verschiedenen Konstruktionen von Kontaktapparaten, die wir im Laufe der Zeit mit Rücksicht auf die Wärmeableitung ausgeführt haben, seien hier nur zwei wiedergegeben. Der Apparat der Abbildung 2 besteht aus einem zylindrischen Blechgefäss, das mit wärmeisolierendem Material umgeben ist. In dem Blechgefäss befinden sich 55, oben offene, dünnwandige Kühlrohre, die unten geschlossen und bis zur halben Höhe mit Methylnaphthalin gefüllt sind. Um die Kühlrohre herum war der Kontakt angeordnet. Die Wirkungsweise des Apparats war folgende: In einem Vorheizer wurde gereinigtes Wassergas auf eine Temperatur von annähernd 200° gebracht, es trat oben in den Reaktionsraum ein, nahm dort genau die Temperatur von 250° an und bewegte sich zwischen den Rohren abwärts durch den Kontakt. Sobald in einem Teil des Kontaktes durch die Reaktionswärme die Temperatur über 250° steigen wollte, sollte das Methylnaphthalin, das bei 250° siedet, sich teilweise in Dampf von der gleichen Temperatur verwandeln und dadurch die Reaktionswärme wegführen. Bis zu einem gewissen Grad entsprach der Apparat auch den Wünschen, aber nicht vollständig.

Nachdem eine ganze Reihe anderer Konstruktionen entwickelt und ausprobiert war, kehrten wir wieder zu einem ähnlichen Prinzip zurück, welches in Abbildung 3 dargestellt ist.

Die Rolle der mit Methylnaphthalin gefüllten Rohre übernahmen hier Druckrohre, die mit Wasser gefüllt sind und die Verbindung zwischen dem oberen und dem unteren Teil eines Röhrenkessels vorstellen. Die Rohre selbst sind mit Aluminium umgossen. In der dadurch entstehenden Platte sind gleichzeitig reihenförmig Kupferbleche eingegossen, zwischen denen sich der Kontakt befand. Wenn der Apparat durch eine elektrische Heizvorrichtung auf die Reaktions-



Verwendet wurde ein Gemisch von Kokereigas und Wassergas in bestimmter Zusammensetzung. Mit einem Gebläse wurde das Gemisch in einen Turm geleitet, in dem es sich mittels warmen Wassers mit Dampf beladen konnte. Die Menge des Wasserdampfes war durch die Temperatur des Rieselwassers gegeben. Dann trat das Gas in einen Methanspalter, in welchem das in dem Gas enthaltene Methan sich an einem Kontakt mit Wasserdampf zu Kohlenoxyd und Wasserstoff umsetzte. Gleichzeitig wurde der grösste Teil der organischen Schwefelverbindungen durch den Wasserdampf zersetzt. Das austretende Gas wurde rasch abgekühlt und hierauf durch Gasreinigungsmasse geleitet. Um den Rest der organischen Schwefelverbindungen zu beseitigen, trat es dann noch durch einen aus Eisenrohren bestehenden Kontaktreiniger, schliesslich wurde das Gas von dem abermals entstandenen Schwefelwasserstoff mit Ferricyankaliumlösung gewaschen. Letztere wird elektrolytisch regeneriert. Das nunmehr ausreichend reine Gas strömt durch eine Gasuhr zum Kontaktapparat, dann durch verschiedene Kühler und einen Entnebler zur aktiven Kohlen. In den beiden Kühlern setzt sich Öl und Reaktionswasser ab, mit der aktiven Kohle wird in üblicher Weise das Leichtbenzin herausgenommen.

Für die wirtschaftliche Durchführung der Benzinsynthese ist es wichtig, möglichst von billigen Gasen auszugehen. Die nachstehende Tafel XII gibt eine Übersicht über verschiedene Gase und Gasmischungen, und zwar sind in der zweiten Spalte die Volumina nutzbares Kohlenoxyd angegeben und in der dritten Spalte die theoretischen Höchstaussbeuten an Benzin in g/cbm.

TAFEL XII.

Ausgangsgas.	Vol.-% nutzbares CO.	Theoretische Höchst- ausbeute an Benzin in g/cbm.
Kokereigas	5.5	34.6
Generator-Mischgas	6.2	39
Kokereigas + Gichtgas		
59.5 + 40.5 %	16.4	103
Kokereigas + Generatormischg		
51.5 + 48.5 %	16.8	105
Spaltgas aus Kokereigas	19.2	121
Spaltgas + Gen. Mischgas		
57.4 + 42.6 %	23.3	147
Spaltgas + Gichtgas		
67.9 + 35.1 %	23.8	150
Wassergas	24	151
Kokereigas + Wassergas		
46.7 + 53.3 %	25.3	159
Spaltgas + Wassergas		
52.5 + 47.5 %	30.4	191

Die nächste Tafel XIII zeigt die in den letzten Jahren geltenden Gaspreise. Die billigste Gasmischung wird demnach erhalten, wenn man einfach Kokereigas und Gichtgas mischt, während, wie aus der vorhergegangenen Tafel ersichtlich ist, die höchsten Ausbeuten aus einem Gemisch von Spaltgas und Wassergas erhalten werden. Wassergas ist aber einstweilen noch ein relativ teures Gas und es ist vorteilhaft, ohne dasselbe auszukommen.

## TAFEL XIII.

*Gaspreise je cbm.*

Kokereigas	5000 WE	1·7 Pfg.
Wassergas	3000 WE	2·0 „
Gichtgas	950 WE	0·3 „

Billigste Gasmischung?

Spaltgaspreis?

Ausbeuten an Benzin in % der Theorie.	Bedarf an WE je kg Benzin.	Kosten der verbrauchten WE in Pfg/kg Benzin, 5000 WE 1·725 Pfg.
100	15000	5·16
50	18725	6·46
30	25750	8·2

## Sichere Belastungen :

Gasreinigung mit Masse 0·05 Pfg/cbm

Regeneration des Ferricyankaliums 2·5 KWH für 10000 cbm Gas.

Wichtig ist auch, dass ausser Benzin keine anderen Produkte in grösserer Menge entstehen, beispielsweise Methan. Nehmen wir an, die Ausbeuten an Benzin seien 100 % der Theorie, d. h. der Verflüssigungsgrad sei 100. Da der Heizwert von 1 kg Benzin rund 12000 Kcal beträgt, so ist auf alle Fälle je kg Benzin eine aus Kohlenoxyd und Wasserstoff bestehende Gasmischung erforderlich, die einen Heizwert von 15,000 Kcal repräsentiert, da beim Übergang des Gases in Benzin 20 per cent vom Heizwert des angewandten Gases in Form von Reaktionswärme entwickelt werden. Wenn 5000 WE 1·7 Pfg kosten, so wird also bei einem solchen Gaspreise das Kilogramm Benzin schon an Rohmaterial über 5 Pfg kosten.

Dieser Betrag steigt, wenn der Verflüssigungsgrad nur 50 per cent. beträgt, auf über 6 Pfg, wenn der Verflüssigungsgrad nur 30 per cent. beträgt, auf über 8 Pfg. Der Grund für diese Steigerung liegt darin, dass eben Kohlenoxyd für unerwünschte Produkte verbraucht wird, bei deren Bildung ebenfalls Wärme frei wird. Diesen Wärme mengen steht aber nicht eine entsprechende Benzinproduktion gegenüber. Die übrigen Kosten der Benzinherstellung werden sich erst bei einem grösseren Versuchsbetrieb beurteilen lassen. Sicher ist aber, dass die Reinigung des Gases mit Masse und die Regeneration des Ferricyankaliums relativ geringe Kosten verursachen. In erster Linie ist, wie schon hervorgehoben, notwendig, dass der Verflüssigungsgrad hoch ist, d.h. dass schon beim einmaligen Überleiten über den Kontakt das Kohlenoxyd möglichst weitgehend in Benzin und Öl umgewandelt wird. Interessant ist in diesem Zusammenhang die Tafel XIV. Aus ihr ersieht man, wie durch mühsame und hartnäckige Arbeit auf dem Wege über tausende von Versuchen der Verflüssigungsgrad mit den verschiedenen Kontakten immer weiter gesteigert worden ist.

## TAFEL XIV.

Zeitliche Entwicklung der Benzinsynthese von Franz Fischer und H. Tropsch.

*Flüssige Produkte (Benzin + Öl) in % der Theorie bei einmaligem Überleiten über den Kontakt.*

Jahr.	Eisen.	Kobalt.	Nickel
1924	...	...	...
1925	ca. 12	ca. 12	...
1925	23	17	Spuren
1927	.		...
1928			...
1929	31	35	...
1930		45	...
1931		71	65
1932			71

Hierzu kommen noch Hartparaffin, aus dem Kontakt extrahierbar, und Gasol.



Besser als Eisen haben sich die Kobaltkontakte bewährt und in den letzten Jahren sind dann infolge einer veränderten Herstellungswiese auch Nickelkontakte hinzugegetreten, die früher für die Benzinsynthese praktisch unbrauchbar erschienen waren. Die Anwendbarkeit der Nickelkontakte bedeutet wegen des niedrigen Preises einen wesentlichen wirtschaftlichen Fortschritt.

Natürlich wird es in den gegenwärtigen Zeiten auch bei weiterer Entwicklung der Benzinsynthese, ebenso wie der I. G. Farbenindustrie A. G. mit ihrem Leuna-Benzin, uns nicht möglich sein, ohne Zollschutz mit dem Auslandsbenzin zu konkurrieren. Das Zustandekommen der Benzinpreise für Auslands und für Inlandsbenzin ist in der Tafel XV dargestellt.

TAFEL XV.

*Zustandekommen des Benzinpreises.*

	Auslands- Pfg/Ltr.	Benzin	Inlands- Pfg/Ltr.
Preis ab Werk in U.S.A.	2·7		
Transport nach Hamburg	3·3		
Preis in Hamburg	6·0		
Kosten beim deutschen Erzeuger			21·6
Zuschlag durch			
Spritbeimischungszwang	1·8	1·8	
Zoll u. Ausgleichsteuer	16·2	1·0	
abzuführen an den Staat	18·0	2·8	
Fracht	1·8	1·4 (Vorzugstarif).	
Händler	8·6	8·6	
Vertrieb	10·4	10·0	
	34·4	34·4	

Man sieht daraus, dass für Auslandsbenzin 18 Pfg/Ltr. an den Staat abgeführt werden müssen, für Inlandsbenzin nur 2·8 Pfg. Ferner genießt das Inlandsbenzin bei der Eisenbahn noch einen Vorzugsfrachttarif. Erwähnt sei an dieser Stelle noch, dass die Bestrebungen, durch direkte Hydrierung der Kohle nach *Bergius* Benzin zu erzeugen, trotz des Zollschatzes wirtschaftlich unmöglich

waren. Es wird heute durch die I. G. Farbenindustrie A. G. in Leuna Benzin durch Hydrierung der *Braunkohle* in technischem Massstabe nicht hergestellt sondern durch Hydrierung von Erdöl und Teeren. Die Anlage der Gesellschaft für Steinkohlenverflüssigung in Meiderich ist schon seit längerer Zeit aus wirtschaftlichen Gründen stillgelegt und in der letzten Zeit hat man auch in England die Kohlenhydrierung als unwirtschaftlich aufgegeben. Das in Leuna erzeugte Benzin\* wird nicht durch Hydrierung von Kohlen, sondern durch Hydrierung von Teeren und Ölen gewonnen, aber selbst bei diesem Verfahren scheint trotz des Zollschatzes kein Gewinn gemacht zu werden.

#### D. 2. Elektrische Verfahren.

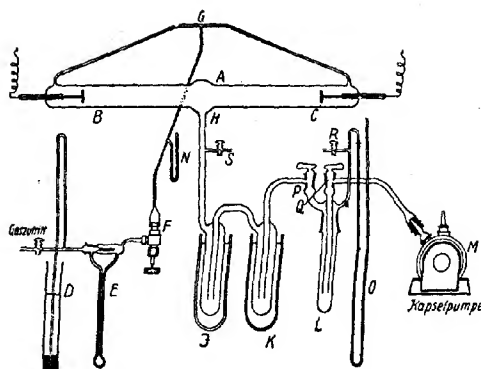
Für die elektrische Umwandlung von Gasen haben wir eine besondere Arbeitsweise unter vermindertem Druck entwickelt. Die Gase werden unter vermindertem Druck durch eine Art grosser Geisslerscher Röhren durchgesaugt und während des Durchganges durch eine Hochspannungsentladung umgesetzt. Ein Teil der in Frage kommenden Reaktionen ist in Tafel XVI zusammengestellt.

#### TADEL XVI.

- (a) bei gewöhnlichem Druck: Lichtbogen, Hochspannungsbogen, Siemens-Röhre, Acetylen, Blausäure, Ozon.
- (b) bei vermindertem Druck nach Franz Fischer u. Peters:
  - 1. Apparatur,
  - 2. Reaktionen: Methan  $\rightarrow$  Acetylen
  - Methan + Stickstoff  $\rightarrow$  Blausäure
  - Methan + Ammoniak  $\rightarrow$  Blausäure
  - Dissoziation der Kohlensäure.

Praktisch wichtig bei diesen Versuchen ist, dass die Abscheidung von Kohlenstoff vermieden wird und dass der Energieverbrauch auf ein Minimum herabgedrückt wird. Bei diesen Reaktionen handelt es sich im wesentlichen und zum mindesten primär im Gegensatz zu den bisher besprochenen katalytischen Verfahren um endotherme Reaktionen, die also nicht Wärme erzeugen sondern verbrauchen. Eine Skizze der verwendeten apparatur ist in Abbildung 5 zu sehen. Das Gas strömt unter Atmosphärendruck durch einen Strömungsmesser zu einem Feinreguliertventil. Dort wird die durchgehende

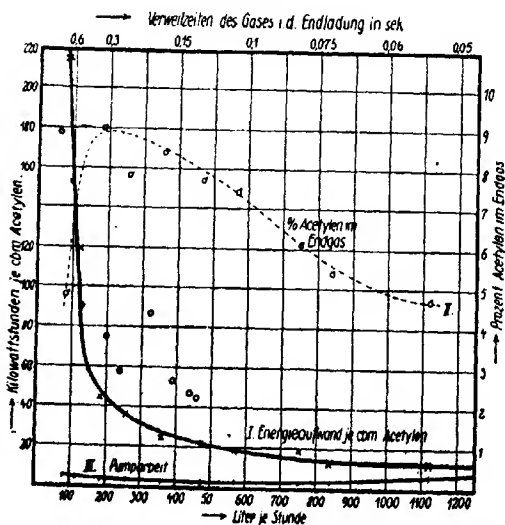
ABB. 5.



Gasmenge so abgedrosselt, dass die auf der rechten Seite der Skizze gezeichnete Ölpumpe den gewünschten Unterdruck zu erzeugen vermag. Von dem Feinregulierungsventil verteilt sich das Gas an den Elektroden und durchströmt von dort die Entladungsröhre von beiden Seiten her. In der Mitte tritt das Gas aus und gelangt durch mit flüssiger Luft gekühlte Vorlagen schliesslich zur Pumpe.

Abbildung 6 gibt einen Überblick über die Bildung von Acetylen aus Methan.

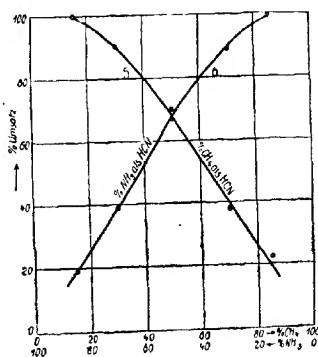
ABB. 6.



Die ausgezogene Kurve 1 zeigt den Energieaufwand pro cbm Acetylen in Abhängigkeit von der Verweilzeit des Gases in Entladungsraum. Man sieht, dass je kürzer die Verweilzeit, also je grösser die Strömungsgeschwindigkeit, dass umso kleiner der Energieaufwand je cbm Acetylen sich erweist. Wie aus der gestrichelten Kurve 2 ersichtlich ist, geht mit abnehmender Verweilzeit die Konzentration des Acetylens im Gase herunter. Begnügt man sich mit einer Acetylenkonzentration im Endgas von 5%, so kommt man zu einem Energieaufwand pro cbm von etwa 13 KWH, dazu kommen noch etwa 5—6 KWH an Pumparbeit.

Abbildung 7 gibt eine Darstellung über die Ausnutzung der beiden Komponenten bei der elektrischen Herstellung von Blausäure aus Ammoniak und Methan. Man sieht daraus, dass bei einer Methan-Ammoniak-Mischung 80 : 20 praktisch sämtliches Ammoniak und bei der umgekehrten Mischung 20 : 80 alles Methan in Blausäure übergeführt werden kann.

ABB. 7.



Die Tafel XVII gibt einige Angaben über die Dissoziation der Kohlensäure bei der elektrischen Unterdruckentladung.

TAFEL XVII.

		CO <sub>2</sub> trocken.	CO <sub>2</sub> feucht.
% Dissoziation	...	40·9	6·2
% Nutzeffekt	...	10·1	1·5
Temperatur gemessen	...	1150°	1165°
Temperatur aus dem Umsatz berechnet	...	2300°	1820°

Durchsatz 150 Ltr/Stde.; Belastung 2 KW.

Saugt man in beschriebener Weise nichtgetrocknete Kohlensäure durch die Entladungsröhre, so wurde unter den gegebenen Bedingungen 6·2% der Kohlensäure in Kohlenoxyd und Sauerstoff zerlegt, und zwar mit einem Nutzeffekt von 1·5%. Der schlechte Nutzeffekt konnte darauf beruhen, dass zwar mehr Kohlensäure dissoziiert wurde, dass aber vor Verlassen des Reaktionsrohres oder kurz danach ein Teil der Dissoziationsprodukte sich wieder vereinigte. Es ist bekannt, dass ganz trockenes Kohlenoxyd mit Sauerstoff schwierig reagiert. Wir haben deshalb die Kohlensäure scharf getrocknet und dann durchgeladen. Unsere Vermutung über die Wiedervereinigung wurde bestätigt, denn nun betrug die Dissoziation 41% und der Nutzeffekt war auf 10·1% gestiegen. Man sieht aus diesem Beispiel, dass auch bei derartigen elektrischen Unterdruckentladungen bessere Ausbeuten erhalten werden können, wenn man dafür sorgt, dass die für die Umsetzung aufgewandte Energie nicht durch rückläufige Reaktionen unnütz verbraucht wird.

#### D. 3. Thermische Verfahren.

Ebenso wie bei den elektrischen Verfahren handelt es sich bei den nachfolgend beschriebenen thermischen um endotherme Reaktionen. Statt elektrischer Energie wird hier rein thermische Energie, also lediglich Wärme zugeführt. Erwähnt seien hier die *Benzolsynthese* aus Methan bei gewöhnlichem Druck und die *Acetylsynthese* aus Methan bei Unterdruck. Bei beiden Synthesen können statt Methan auch Homologe desselben verwendet werden. Die Synthesen aus Methan haben aber ihrer Neuheit und ihrer umfassenden Anwendungsfähigkeit wegen besonderes Interesse. Die in Frage kommenden Wärmetönungen sind nachfolgend zusammengestellt:

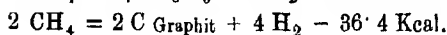
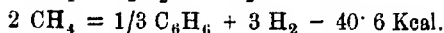
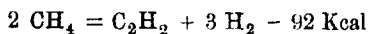
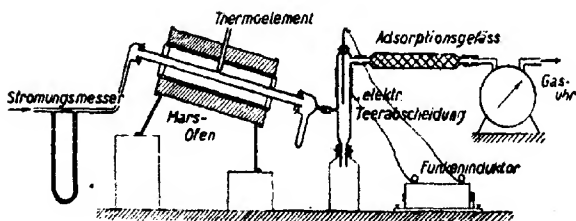


ABB. 8.

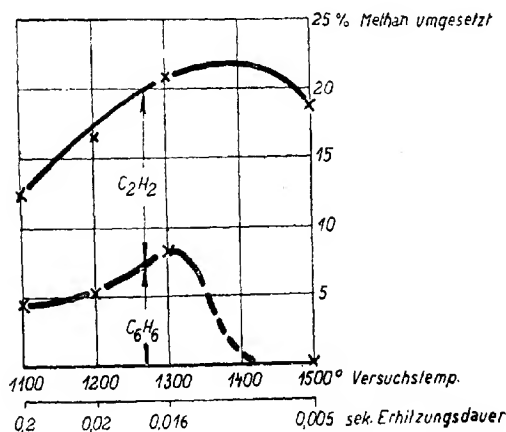


Die für die Benzolsynthese benutzte Laboratoriumsapparatur ist in Abbildung 8 skizziert.

Das Methan durchstreicht zunächst einen Strömungsmesser, dann ein Rohr aus Pythagorasmasse, welches in einem sogenannten Mars-Ofen erhitzt wird, dann einen elektrischen Teerabscheider, ein Gefäß mit aktiver Kohle und schliesslich eine Gasuhr. Vor und in dem elektrischen Teerabscheider setzen sich die hochsiedenden Produkte ab, in der aktiven Kohle wird das Benzol aus dem Reaktionsgas herausgenommen.

Abbildung 9 zeigt zwei Kurven, welche die Prozente des umgesetzten Methans angeben in Abhängigkeit von der Versuchstemperatur, und zwar jeweils bei der für die betreffende Versuchstemperatur günstigsten Erhitzungsdauer.

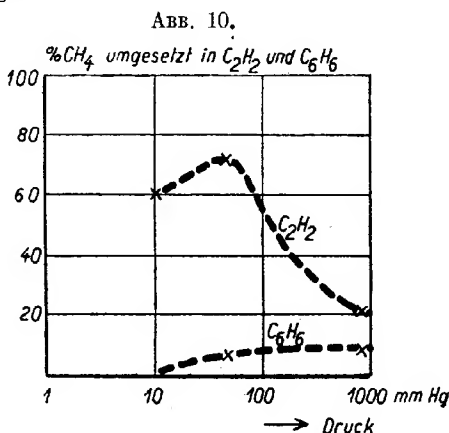
ABB. 9.



Die untere für Benzol gültige Kurve zeigt, dass bei etwa 1300° und einer Erhitzungsdauer von 0.016 Sekunden ungefähr 8% des Methans in Benzol bei einmaligem Durchsatz umgewandelt wurden. Bei etwa 1400° war die zu Benzol umgesetzte Menge Methan nur noch geringfügig. Die senkrechten Abstände zwischen der unteren und oberen Kurve lassen die Prozente Methan erkennen, welche gleichzeitig in Acetylen umgewandelt wurden. Man erkennt, dass bei etwa 1300° rund 13% des Methans in Acetylen verwandelt wurden. Bei 1400° betrug der Prozentsatz 22%, während, wie schon erwähnt, gleichzeitig Benzol nicht mehr entstand. Wenn man annimmt, dass das Acetylene vor dem Benzol entsteht und das Benzol sich aus dem Acetylen während der Abkühlungsperiode bildet, so kann man sich

vorstellen, das bei der bei 1400° angewandten geringen Erhitzungsdauer, die etwa auf 0.08 Sekunden zu schätzen ist, unter den gewählten Arbeitsbedingungen die Zeit zur nachträglichen Benzolbildung nicht mehr ausgereicht hat.

Während die Kurven der Abbildung 9 die Verhältnisse bei Atmosphärendruck wiedergeben, erkennt man aus Abbildung 10 den Einfluss des Druckes auf die Bildung von Acetylen und von Benzol bei konstant gehaltener Temperatur und für gleiche Strömungsgeschwindigkeiten.



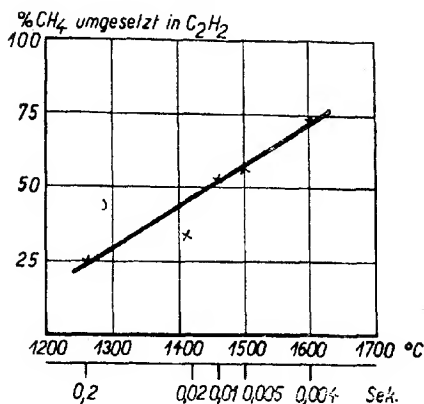
Verfolgt man den Lauf der Kurve von 10 mm Quecksilberdruck bis zu 1000 mm, so sieht man, dass die Benzolkurve von 1% igem Umsatz bis zu 8% igem erst schneller und dann langsamer ansteigt. Die Acetylenkurve setzt bei 10 mm Druck bereits mit 60% igem Methanumsatz ein, erreicht über 70% bei etwa 50 mm und fällt dann mit wachsendem Druck ab. Bei 1000 mm wird nur noch 20% des Methans in Acetylen umgesetzt.

Es zeigt sich also, dass für die thermische Herstellung von Acetylen verminderter Druck vorteilhaft ist, während man annehmen darf, dass für die Umwandlung des Acetylens in Benzol oder allgemeiner ausgedrückt, für die thermische Benzolbildung die Anwendung verminderten Druckes keine Vorteile bietet.

Die Kurven der eben besprochenen Abbildungen zeigen, den Umsatz bei Verwendung von reinem Methan. Abbildung 11 gibt die Verhältnisse bei Verwendung von Kokereigas.

Kokereigas enthält etwa 25% Methan; als Verdünnungsmittel kommt in erster Linie dabei Wasserstoff in Betracht. Die Kurve, ungefähr eine gerade Linie, zeigt, wieviel Prozent des im Kokereigas

Abb. 11.



enthaltenen Methans in Acetylen umgewandelt wird bei den verschiedenen Temperaturen und den dazu gehörigen optimalen Erhitzungszeiten. Man sieht, dass bis  $\frac{3}{4}$  des im Kokereigas enthaltenen Methans bei 1600° und einer Erhitzungsdauer von 0.004 Sekunden in Acetylen umgewandelt werden können. Die Versuche sind bei Atmosphären druck ausgeführt, der günstige Effekt beruht z. T. darauf, dass mit einem niedrigen Methanpartialdruck gearbeitet wurde.

Von der Umwandlung des Acetylens in Benzol bei der thermischen Benzolsynthese aus Methan habe ich bereits gesprochen. Sicherer und mit grösseren Ausbeuten lässt sich diese Umwandlung beherrschen, wenn sie getrennt von der Acetylendarstellung ausgeführt wird. Ich möchte hier nur erwähnen, dass sich dafür Temperaturen von 600 bis 700° und dass sich Katalysatoren, beispielsweise aktive Kohle und Silica-Gel bewährt haben. Die Gegenwart kleiner Mengen von Kohlensäure hat sich für die Polymerisation als vorteilhaft erwiesen. Eine andere Art von Polymerisation des Acetylens, die bei Gegenwart von Wasserstoff und Nickel—oder Eisenkatalysatoren sich voll zieht, ist von *Sabattier* beobachtet worden. Hierbei entstehen durch die Mitwirkung des Wasserstoffs benzinartige Kohlenwasserstoffe. Neuere Untersuchungen aus unserem Institut haben ergeben, dass es sich dabei hauptsächlich um Olefine handelt und dass diese Synthese mit ungereinigtem elektrisch durchladenen Kokereigas unter Verwendung von Fe—Ni (10 : 1) als Kontakt sich leicht durchführen lässt. Auf die unzähligen anderen Anwendungen und chemischen Verarbeitungen des Acetylens kann hier nicht eingegangen werden.



D. 4. *Biologische Methoden.*

Zum Schluss sei noch der biologischen Methoden gedacht, welche zur Umwandlung von Gasen dienen können. *Söhngen* hat im Jahre 1910 gezeigt, dass sich unter der Einwirkung von Grabenschlamm bzw. der darin enthaltenen Bakterien Kohlensäure mit Wasserstoff zu Methan vereinigt. Obwohl man hätte denken, dass eine entsprechenden Umwandlung des Kohlenoxyds mit Wasserstoff in Methan wegen der Giftigkeit des Kohlenoxyds nicht möglich sei, sind entsprechende Versuche doch positiv ausgelaufen. Zur Verwendung gelangte erst Emscherschlamm mit den darin befindlichen Bakterien. Später wurden die Versuche auch mit reinen Kulturen mit Erfolg ausgeführt. Wenn es gelingen würde, die Geschwindigkeit dieser biologischen Umsetzung des Kohlenoxyds zu Methan ausreichend zu beschleunigen, so könnte an eine praktische Ausnutzung, beispielsweise zur *Leuchtgasentgiftung* gedacht werden. Nähere Untersuchungen über diese Reaktionen sind noch immer im Gange. Einstweilen haben sie gezeigt, dass die Reaktion anscheinend so verläuft, dass zuerst aus der Feuchtigkeit und Kohlenoxyd, Kohlensäure und Wasserstoff entstehen und dass dann zum mindesten ein Teil der Reaktion aus Kohlensäure und Wasserstoff Essigsäure bildet. Am Schluss wird dann die Essigsäure in Methan übergeführt. Diese biologischen Umwandlungen der Gase sind erst neuesten Datums und dementsprechend erst im Anfang ihrer Entwicklung. Aber sie sind zum mindesten wesentlich von grossem Interesse und sollten deshalb nicht vergessen werden.

Die Verwertung der Kohle auf dem Wege über die Gase zeigt schon heute eine grosse Zahl von Möglichkeiten. Wie wird es erst einige Jahrzehnte später aussehen! Der Vorteil der Verwertung der Kohle auf dem Wege über die Gase besteht aber nicht nur in der Fülle der Möglichkeiten. Ganz gleichgültig, ob katalytische oder elektrische oder thermische oder biologische Verfahren Anwendung finden, die dazu notwendigen Gase lassen sich mehr oder weniger vorteilhaft aus sämtlichen festen Brennstoffen herstellen und darin liegt ein grosser Vorteil, die allgemeine Anwendbarkeit der Brennstoffverwertung auf dem Wege über die Gase.

Kurze Zusammenstellung der dem Vortrag zugrunde liegenden Veröffentlichungen aus dem Kaiser-Wilhelm-Institut für Kohlenforschung Mulheim-Ruhr (Eine vollständige Literaturübersicht findet sich in den angegebenen Arbeiten).

#### I. Benzinsynthese.

##### (a) Gasbeschaffung.

Die Umwandlung von Methan in Wasserstoff und Kohlenoxyd. (Franz Fischer, H. Tropsch, W. Ter-Nedden u. A. Franschke, *Brennstoff-Chem.*, 1928, 9, 39.

##### (b) Gasreinigung.

Über die Auswaschung von Schwefelwasserstoff aus industriellen Gasen mit Hilfe von alkalischen Ferricyankaliumlösungen. (Franz Fischer u. P. Diltbey, *Brennstoff-Chem.*, 1928, 9, 122.

Über die Bestimmung, Umwandlung und Entfernung des organisch gebundenen Gasschwefels. (O. Roelen, *Brennstoff-Chem.*, 1931, 12, 305.

##### (c) Synthese.

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Stand Ende 1930: Franz Fischer, *Brennstoff-Chem.*, 1930, 11, 439

Neuester Stand: Franz Fischer u. K. Meyer, *Brennstoff-Chem.*, 1931, 12, 225; Franz Fischer u. H. Koch, *Brennstoff-Chem.*, 1932, 13, 61.

##### (d) Verschiedene andere Arbeiten.

Zusammensetzung des synthetischen Benzins. (H. Tropsch u. H. Koch, *Brennstoff-Chem.*, 1929, 10, 337).

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#### II. Synthese von Synthol.

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#### III. Herstellung von Kohlenstoff aus Kohlenoxyd.

Franz Fischer u. P. Diltbey: *Brennstoff-Chem.*, 1927, 8, 388; 1928, 9, 24.

IV. Thermische Synthese der Benzol und Acetylenkohlenwasserstoffe aus Methan.

## aus Methan.

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K. Peters u. K. Mayer, *Brennstoff-Chem.*, 1929, 10, 324; Franz Fischer u. H.  
Pichler, *Brennstoff-Chem.*, 1930, 11, 501.

## V. Umwandlung von Acetylen in flüssige Kohlenwasserstoffe.

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Blausäurebildung. (K. Peters u. H. Küster, *Brennstoff-Chem.*, 1931, 12, 122, 329.

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Biologische Umsetzungen des Kohlenoxyds. Franz Fischer, R. Lieske u. K. Winzer, *Brennstoff-Chem.*, 1931, 12, 193.

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